compacted foot moisture █████t insulating materials. The compact█████nsulating material also allows for rapid conduction of he██ away from the foot by the presence of excessive moisture. In some cold weather boots, foot moisture is allowed to collect and freeze directly below the foot insulating layer. Once foot moisture collects and freezes, it can form a conducting path for heat to leave the boot. Frostbite results when the foot is allowed to remain in prolong extreme cold conditions. Unless the moisture latent socks and any frozen moisture inside the boot and below the insulating layer are removed and the foot is kept warmed and dried, the water in the foot is in danger of freezing into crystals of ice. The need to protect the foot also applies to the other parts of the human skin that may be exposed to the cold, such as the face, the neck, the fingers, the nose, the ears, and other parts of the body.

US Patent 3,660,849 discloses a insulative deep submergence diving suit based on a flexible supporting surface layer substantially fully covering a very low modulus gel of SIS and SBS block copolymer-mineral oil and glass microbubble filler. The problem with such a gel suit made from a SIS and SBS is that the suit can easy break apart, rip, or tear under its own weight without the flexible support. The flexible support covering the inside surface of the suit also isolates the gel.

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SUMMARY OF THE INVENTION

I have unexpectedly discovered insulating elastic gel compositions, insulating gel composites, and insulating gel articles for protecting the skin of the human body from cold, which acts as a body insulator. Parts of the skin which can be advantageously protected by the insulating gels and gel composites of the invention include the face, the fingers, the hand, the nose, the ears, the foot and the like. The insulating gels and gel composite are of advantage for forming articles for the human body exposed to extreme cold environments such as encountered in mountain climbing, in outer space, in the deep oceans, and beneath the below zero waters and on wind swept lands 60° north and south latitudes encompassing the polar regions of the Arctic and Antarctic circles.

The insulating elastic gels, insulating gel composites, and insulating gel articles of the invention comprises: (i) one or more layers of the same or different insulating elastic gels, having one or more integral homogenous or inhomogeneous insulating components dispersed in said gel in combination with or without (ii) one or more layers of elastic gels or one or more gel composite layers, wherein (i) or (ii) with or without (iii) one or more layers of a fabric, a polymeric open cell foam or a polymeric closed cell foam; wherein (i), (ii), or (iii) in combination with or without (iv) one or more hydrophilic moisture absorbing and retaining layers or patches between said insulating elastic gel layer and skin, said elastic gel layer, or said composite gel layer and one or more layers of a fabric or a polymeric open cell foam; said insulating gel and composite gel being in direct selected contact with the skin and capable of substantially preventing the skin from generating moisture. Moreover, the insulating gel and insulating gel composites are highly tear resistant, fatigue resistant, soft and strong and advantageously useful in direct gel contact with the skin protecting it from extreme cold.

The present inven█takes a completely different direc█from the design and function of the prior art. The insulating gels of the cold weather wear (Figs. 15-28) such as boots, face mask, gloves, full body wear, and the like have as an essential, direct contact with the skin of the body. The present invention is directed to cold weather body wear such as boots, face mask, gloves, and full body wear (for work or play) capable of substantially preventing, controlling or selectively facilitating the production of moisture from selected parts of the skin of the body such as the forehead, neck, foot, underarm, etc.

With respect to the footwear of my invention, it is advantageously useful for protecting the skin of the foot from frostbite in extreme cold weather. This is accomplished in four ways: thermally insulating the barefoot, providing a non-compacting material for non-constricting blood flow in the foot by dissipating impact and shock to the foot, and reduce or substantially eliminate or prevent the production of foot moisture by the barefoot. The barefoot, for example, can be protected advantageously from extreme cold by using the insulating gel or insulating gel composites (Figs. 1-14b) of the invention. The footwear of my invention for protecting the skin of the foot in cold weather comprises: (I) an outer boot (16); (II) one or more dimensionally stable substantially hydrophobic insulating gel sock (15) (Fig. 15) or a gel composite sock (18) (Figs. 16-19) impregnated with one or more dimensional stable substantially hydrophobic insulating gels disposed in said boot and formed of a material and in sufficient amounts capable of removablely encapsulating and integrally in sealing contact with the skin of the foot and one or more toes of the foot so as to substantially displace the air surrounding the skin of the foot and substantially prevent the production of moisture from the skin of said foot, and

(III) a thermal insulation member (17) disposed between said gel sock (15) or gel composite sock (18) and said boot; said gel is a elastic gel, a non-elastic gel, a solid gel, a foamed gel, an open cell gel, or a closed cell gel; said gel in combination with or without one or more antiperspirant agents, deodorant agents, antibacterial agents, antifungal agents, and hydrophobic agents; said gel being capable of allowing equal distribution of foot pressure and non-constriction of blood circulation in the foot.

The footwear comprises a outer boot (16) with or without a rigid structural member to provide for vertical stability about the ankle areas. The outer boot can be made from any suitable boot material. Depending on the nature of the activity, the outer boot (16) can be made from any man made or natural strong, tough, flexible water repellent material, including plastics, hydrophobic treated leathers, natural or man made rubbers, thermoplastic elastomers, hydrophobic treated fabrics, metals, silicone rubbers, polyurethane elastomers, other water repellent strong, tough, flexible polymeric materials, or a combination thereof. Material suitable for forming the outer boot include polyethylene, polyethylene copolymers, polypropylene, polypropylene copolymers, high impact polystyrene, polystyrene copolymers, polyvinlycloride, polyurethane, polybutylene, polycarbonate, polyester, polyimide, polyvinylidene chloride, acrylonitrile copolymers, and the like.

In addition to the outer boot, a thermal insulation member (17) is disposed inside the boot. The thermal insulation member inside of the boot comprises one or more thermally insulating material layers. The insulating material layers can be one or more layers of any suitable natural or man made thermally insulating materials including: close cell foams, open cell foams, materials containing insulating particles (microspheres), natural hairs, natural and synthetic wools, cotton, and the

like. The thickness of t██nsulating member (17) layered mater██ can be less than 1 cm to 3 cm or greater depending on the degree of insulation required.

Between the barefoot and the insulating member (17) layers, the foot is surrounded by one or more dimensionally stable substantially hydrophobic thermally insulating gel (15) sock or a gel composite sock (18, 23, 22). The gel composite sock is formed from any suitable material, M_n, impregnated with one or more dimensional stable substantially hydrophobic thermally insulating gels, G_n. The gel sock (15) or gel composite (18, 23, 22) sock is disposed in the boot for receiving and surrounding the barefoot and formed of a material and in sufficient amount capable of removablely encapsulating and integrally in sealing contact with the skin of the foot and one or more toes of the foot so as to substantially displace the air surrounding the barefoot and substantially prevent the production of moisture from the skin of said foot. The gel, G_n, where n denotes a elastic gel, a non-elastic gel, a solid gel, a foamed gel, an open cell gel, or a closed cell gel; said gel in combination with or without one or more antiperspirant agents, deodorant agents, antibacterial agents, antifungal agents, and hydrophobic agents; said gel being capable of allowing equal distribution of foot pressure and non-constriction of blood circulation in the foot. The gel, G_n, can be a silicone gel, a urethane gel, a thermoplastic elastomer gel or a combination thereof. Such gels are capable of "wetting" the surface of the skin so as to prevent the generation of body moisture. Of greatest advantage is the us o of selected thermoplastic elastomer gels which are tear resistant and fatigue resistant. The gel can be made additionally more insulating by incorporating open cell voids or closed cell voids (man made microspheres) forming a gel foam (22) sock having reduced weight. In the case of open cell gels, the gel on the inside of the boot facing the skin surface is made to have a thick continuous, un-broken gel surface so as to prevent air from contacting the skin of the foot.

The gels mentioned herein which are of advantage are strong, tear resistant, fatigue resistant, soft, pliable, and capable of removablely encapsulating and in sealing contact with the skin of the foot so as to substantially displace the air surrounding the skin surface of the foot and prevent air from contacting the skin of the foot.

For most purposes, such as boots for walking on level polar ice or frozen tundra in the Arctic, on level Antarctic terrain, or on the level deck of an ice breaker, a thin layer of gel (15) is adequate to encapsulate and seal the skin of the foot from air and prevent the production of foot moisture. In the case of active sports, such as a ski boots or hunting boots, a gel laminated (18) sock is disposed in the boot with the gel side encapsulating and sealing the skin of the foot from air and prevent the production of foot moisture.

For the average climbing boots, a multi-interwoven layered sock is disposed in the boot. The inner top layers of the interwoven, multi-layered sock is impregnated with sufficient amounts of gel (25) so as to form a stable support and sufficient for encapsulating and sealing the skin of the foot from air and prevent the production of foot moisture. In the case of rugged mountain climbing boots that requires a highly more stable boot inner support, the top few millimeter of surface of a natural or synthetic dense batting material, a dense open cell foam, or a felt material can be use to form the bottom of the inner gel (26) sock disposed in the boot. The top layer of the inner sock surface is impregnated with gel (24) forming a highly stable support and capable of encapsulating

and sealing the skin of ● foot from air and prevent the produ ● of foot moisture. In all cases, sufficient gel is present in the areas under, over and between the toes to insulate and provide a sealing contact of the gel with the skin in and about the toe region to encapsulate and seal the skin surrounding the toes from air and prevent the production of foot moisture.

As contemplated, (15) is G_n or the composite of Fig. 11. The gel composite layers denoted by (18), (23), (24), and (26) are illustrated by Figs. 1-3, 8-14b. The composite (22) is illustrated by Figs. 8-10A, and 11-14a.

Moreover, the gel sock or gel composite sock for receiving and surrounding the foot can be further separated from the insulating layer by a barrier, such as a polymeric membrane or film keeping one or more components of the gel or agents from migrating into the insulating layer.

In general, the boot, the outer boot shell, the boot ankle support joint, the sole, the insulating layer, and gel sock are designed to take into account the gait cycle. The subtalar or heel joint allows the foot to dissipate the forces generated while walking. The positions of the heel while walking are supination, neutral, pronation, returning to neutral and then to the supination position. In part, the gel and gel composites will help greatly dissipate the force generated by walking. Walking in extreme cold ice or snow weather conditions can be very slow.

Likewise, the hands and fingers can be protected against frostbite by using insulating gel and insulating gel composite lined gloves (Figs. 20-22). The face is also protected by using insulating gels and gel composites forming the head, face, and neck masks (Figs. 23-28). The composites of Figures 1-14b are of advantage for protecting the head, face and neck. Perforations (Figs. 24-28) can be form in the gel or gel composite insulating layers at the regions of the nose, mouth, and ear. Oxygen breathing connections (13) can be formed as an integral part of the insulting mask (Figure 24). Inner water absorbent patches can be inserted through slits at (11) at the forehead, neck, (of the mask) and other parts of the body in a gel composite body suite such as at the underarm regions and torso, back, arms (not shown in the drawings). The patches can be easy inserted and removed through the slits as desired. The patches can be placed selectively almost anywhere about the body while the remainder parts of the body are prevented from generating body moisture. The hydrophilic patches can be made from any moisture adsorbing material capable of absorbing at least 50% of its weight of water. Such hydrophilic materials include, natural materials (cotton) or water absorbing polymers, hydrogel forming polymers, salt tolerant super absorbent (US Patent 5274018), starch modified adsorbents (US Patent 4103062 and 3938522), polysaccharide (starch or cellulose modified polymers). These and other water absorbing materials such as disclosed in US patents: 5,599,335; 5536264, 5532350, 5505718,5422169,5419956, 5397626, 5330822,5180622, 5149334, 5147343, 5143680, 4921904, 4892533, 4824901, 4813945, 4755178, 4755562, 4605401, 4429001, 4366294, 378872, and the like are herein incorporated by reference. The hydrophilic patches are held in place by the gel on one side and in direct contact with the skin. In the case where direct contact of the patches to the skin is not desirable, the patches or hydrophilic materials can be place in slit pockets between the gel or gel composite layer and a foam pocket or fabric pocket layer facing the skin. The gel or gel composite pocket layers of advantage for inserting the hydrophilic patches include gel layer-pocket-foam layer, gel or gel composite layer-pocket-fabric layer. The pockets for receiving the hydrophilic patches are formed by placing cut blanks of the shape and size of the intended patches between the gel and form or gel and fabric layers before laminating. After the

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lamination is complete, ● or more slits are cut from the gel ● side to remove the cut blanks. The slit cuts are made overlapping the blanks so that when the patches are inserted, the slits are on the overlapped portion of the patches. The side of the patches facing away from the skin can also be coated with a gel to provide for insulating sealing at the slits when inserted into the pockets.

In the eye area, corrective lens (fig, 25) or wide view visor (Figs. 26-28) can be incorporated as a tri-layer of $M_nG_nM_n$ (Fig. 10b) or $G_nM_nG_n$ (Fig. 14b). The visor layers include polystyrene layer/gel layer/polystyrene layer, polycarbonate layer/gel layer/polycarbonate layer, crystalline polypropylene layer/gel layer/polypropylene layer, clear silicone layer/gel layer/silicone layer, and the like.

The (G_nM_m), (M_n dispersed in G_n), layer is made from a low concentration to a high concentration of insulating microspheres. As for purpose of distinction, the low to moderate concentration of microspheres in the gel is referred to insulating gels. The highly concentrated microsphere containing gels also have the attribute of being fluffy and light. These are also referred to as fluffy, light, soft, airy compositions. The high concentration dispersion fluffy, light, soft, airy, solid, strong elastic gelatinous elastomer composition, (G_nM_m), exhibiting substantially complete resistance to elastic deformation, capable of substantial complete shape-memory recovery and being dimensionally stable, wherein when n is a subscript of G, n denotes the same or a different gel rigidity. The gel of the invention is formed from (I) 100 parts by weight of at least one or more high viscosity block copolymer; (II) about 300 to about 1,600 parts by weight of a plasticizing oil; and in combination with or without (IV) and (V) described below. The fluffy, elastic solid gelatinous elastomer composition, (G_nM_m), is made from (I), (II), and (III) a selected amount of one or more heat expandable plastic or synthetic particulate material dispersed in an ordered, random, homogeneous, nonhomogeneous, stratified, partially stratified or one or more separated phases and in combination with or without (IV) and (V) described below. The dispersed particulate material is capable of producing a predetermined volume of closed cell particulate dispersion forming said (G_nM_m) having a density of from about 0.80 g/cm^3 to less than about 0.60 g/cm^3, a gel rigidity of from about 20 to about 3,000 gram Bloom, and an elongation of at least 200%.

The G_n and M_n can be in adhering contact, laminated or physically interlocked with a selected material M_n to form a composite comprising combinations of G_n and M_n any sequential additions or permutations of said combinations G_nG_n, M_nG_n, $G_nM_nG_n$, $M_nG_nM_n$, $M_nG_nG_n$, $M_nM_nG_n$, $M_nG_nG_nG_n$, $M_nM_nM_nG_n$, including $M_nG_nG_nM_n$, $G_nM_nG_nM_n$, $G_nG_nM_nG_n$, $M_nG_nM_nM_n$, $M_nG_nM_nG_n$, $G_nM_nG_nG_n$, $G_nM_nM_nG_n$, $G_nG_nM_nG_nM_n$, $G_nG_nM_nG_nM_n$, $G_nM_nG_nG_nM_nM_n$, $G_nM_nG_nG_nM_nG_n$, $G_nM_nM_nG_nG_n$, $G_nG_nG_nM_nG_nG_n$, $M_nG_nG_nM_nG_n$, $M_nG_nM_nG_nM_n$, $G_nG_nM_nM_nM_n$, $G_nM_nM_nG_nM_n$, $G_nG_nG_nM_nG_nG_n$, $G_nM_nG_nM_nM_n$, $G_nM_nM_nG_nM_nG_n$, $G_nG_nM_nG_nM_nG_n$, $G_nM_nG_nM_nG_nM_n$, $G_nM_nM_nG_nM_nG_n$, $G_nG_nM_nM_nG_nG_n$, $M_nG_nG_nM_nG_nG_n$, $M_nM_nG_nG_nM_nM_n$, $M_nG_nG_nM_nG_nM_n$, $M_nG_nG_nM_nG_nG_n$, $G_nG_nM_nG_nG_nM_n$, $G_nM_nG_nM_nG_nM_n$, $M_nM_nM_nG_nM_nM_nM_n$, $M_nG_nM_nG_nG_nM_n$, $G_nM_nG_nM_nG_nM_nG_n$, $M_nG_nM_nG_nM_nM_nG_n$, $G_nM_nM_nG_nM_nM_nG_n$, $M_nG_nG_nM_nG_nG_nM_n$, $G_nM_nG_nM_nG_nM_nG_nM_n$, $G_nG_nM_nM_nG_nG_nM_n$, $G_nG_nM_nG_nG_nM_nG_n$, $M_nG_nG_nM_nG_nG_nM_n$, $G_nM_nG_nG_nM_nG_nG_nM_nG_n$, $G_nG_nM_nG_nM_nG_nM_nG_nG_n$, $G_nM_nG_nM_nG_nM_nG_nM_nG_nM_nG_nM_nG_nM_nG_n$ or combinations thereof.

The (G_nM_m) can be in adhering contact, laminated or physically interlocked with a selected G_n, (G_nM_m) or material M_n to form a composite comprising combinations of (G_nM_m) any sequential additions

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or permutations of said ● inations of (G_nM_m), $(G_nM_m)(G_nM_m)$, $(G_●_n$, $M_n(G_nM_m)$, $M_nM_n(G_nM_m)$, $M_nG_nG_n(G_nM_m)$, $M_nM_nM_n(G_nM_m)$, including $M_nG_n(G_nM_m)$, $(G_nM_m)G_nM_n$, $G_n(G_nM_m)G_n$, $M_n(G_nM_m)M_n$, $M_n(G_nM_m)G_n$, $(G_nM_m)G_nG_n$, $(G_nM_m)M_nG_n$, $G_n(G_nM_m)G_nM_n$, $(G_nM_m)G_nM_nM_n$, $(G_nM_m)G_nM_nG_n$, $(G_nM_m)M_nG_nG_n$, $G_nG_n(G_nM_m)M_n$, $M_nG_n(G_nM_m)G_n$, $M_n(G_nM_m)(G_nM_m)$, $G_n(G_nM_m)M_nM_n$, $(G_nM_m)M_n(G_nM_m)$, $G_nG_n(G_nM_m)G_nG_n$, $M_n(G_nM_m)(G_nM_m)G_n$, $G_n(G_nM_m)M_nG_n$, $G_n(G_nM_m)(G_nM_m)G_n$, $(G_nM_m)(G_nM_m)(G_nM_m)$, $(G_nM_m)M_nG_n(G_nM_m)$, $M_nG_n(G_nM_m)(G_nM_m)$, $G_n(G_nM_m)M_nG_nG_n$, $M_nM_nG_n(G_nM_m)M_n$, $M_nG_n(G_nM_m)(G_nM_m)$, $M_nG_n(G_nM_m)G_nG_n$, $G_n(G_nM_m)G_n(G_nM_m)$, $(G_nM_m)(G_nM_m)G_n$, $M_nM_nM_n(G_nM_m)M_nM_n$, $M_n(G_nM_m)G_n(G_nM_m)$, $M_n(G_nM_m)(G_nM_m)M_nG_n$, $(G_nM_m)M_n(G_nM_m)M_nG_n$, $M_nG_n(G_nM_m)G_n(G_nM_m)$, $M_nG_n(G_nM_m)G_n(G_nM_m)$, $(G_nM_m)(G_nM_m)(G_nM_m)G_n$, $G_n(G_nM_m)M_nG_n(G_nM_m)M_n$, $G_n(G_nM_m)G_n(G_nM_m)G_nG_n$, $(G_nM_m)(G_nM_m)(G_nM_m)(G_nM_m)$, $(G_nM_m)G_n(G_nM_m)G_n(G_nM_m)G_n$, $G_n(G_nM_m)(G_nM_m)(G_nM_m)G_nG_n$, or $(G_nM_m)(G_nM_m)(G_nM_m)(G_nM_m)(G_nM_m)G_n$.

The (I) block copolymer component(s) forming the G_n of the invention is a linear, multi-arm, branched, or star shaped copolymer of the general configuration
poly(styrene-ethylene-butylene-styrene), poly(styrene-ethylene-propylene-styrene), poly(styrene-ethylene-styrene), poly(styrene-butylene-styrene), poly(styrene-ethylene-ethylene/butylene-styrene), poly(styrene-ethylene-ethylene/propylene-styrene), poly(styrene-butylene-ethylene/propylene-styrene), poly(styrene-butylene-ethylene/butylene-styrene), poly(styrene-ethylene-ethylene/propylene-ethylene-styrene), poly(styrene-ethylene-ethylene/butylene-butylene-styrene), poly(styrene-butylene-ethylene/propylene-butylene-styrene), poly(styrene-butylene-ethylene/butylene-butylene-styrene), poly(styrene-ethylene-butylene-ethylene/butylene-styrene), poly(styrene-ethylene-butylene-ethylene/propylene-styrene), poly(styrene-ethylene/butylene-ethylene/propylene-styrene), poly(styrene-ethylene-ethylene/butylene-ethylene/propylene-styrene), poly(styrene-ethylene-ethylene/propylene-ethylene/butylene-styrene), poly(styrene-butylene-ethylene/butylene-ethylene/propylene-styrene), poly(styrene-butylene-ethylene/propylene-ethylene/butylene-styrene), poly(styrene-ethylene-ethylene/propylene-ethylene-ethylene/propylene-styrene), poly(styrene-ethylene-ethylene/propylene-ethylene-ethylene/butylene-styrene), poly(styrene-ethylene/propylene-butylene-ethylene/propylene-styrene), poly(styrene-butylene-ethylene/butylene-butylene-ethylene/butylene-styrene), poly(styrene-butylene-ethylene/butylene-butylene-ethylene/propylene-styrene), poly(styrene-ethylene-ethylene/butylene-butylene-ethylene/propylene-styrene), poly(styrene-ethylene-ethylene/propylene-butylene-ethylene/butylene-styrene), poly(styrene-ethylene-ethylene/propylene-ethylene-ethylene/propylene-ethylene-styrene), poly(styrene-butylene-ethylene/propylene-butylene-ethylene/propylene-butylene-styrene), poly(styrene-ethylene-ethylene/propylene-ethylene-ethylene/butylene-styrene), poly(styrene-ethylene-ethylene/propylene-ethylene/butylene-styrene), poly(styrene-ethylene-ethylene/propylene-ethylene-ethylene/propylene-ethylene/butylene-styrene), poly(styrene-ethylene-ethylene/propylene-ethylene-ethylene/propylene-ethylene-styrene), poly(styrene-ethylene-ethylene/propylene-ethylene-ethylene/butylene-ethylene/propylene-ethylene/butylene-butylene-styrene),
poly(styrene-ethylene-butylene)$_n$, poly(styrene-ethylene-propylene)$_n$, poly(styrene-ethylene)$_n$, poly(styrene-butylene)$_n$, poly(styrene-ethylene-ethylene/butylene)$_n$, poly(styrene-ethylene-ethylene/propylene)$_n$, poly(styrene-butylene-ethylene/propylene)$_n$, poly(styrene-butylene-ethylene/butylene)$_n$, poly(styrene-ethylene-ethylene/propylene-ethylene)$_n$, poly(styrene-ethylene-ethylene/butylene-butylene)$_n$, poly(styrene-butylene-ethylene/propylene-butylene)$_n$, poly(styrene-

butylene-ethylene/buty le⬤tylene)$_n$, poly(styrene-ethylene-bu⬤e-ethylene/butylene)$_n$,
poly(styrene-ethylene-butylene-ethylene/propylene)$_n$, poly(styrene-ethylene/butylene-
ethylene/propylene)$_n$, poly(styrene-ethylene-ethylene/butylene-ethylene/propylene)$_n$, poly(styrene-
ethylene-ethylene/propylene-ethylene/butylene)$_n$, poly(styrene-butylene-ethylene/butylene-
ethylene/propylene)$_n$, poly(styrene-butylene-ethylene/propylene-ethylene/butylene)$_n$, poly(styrene-
ethylene-ethylene/propylene-ethylene-ethylene/propylene)$_n$, poly(styrene-ethylene-ethylene/propylene-
ethylene-ethylene/butylene)$_n$, poly(styrene-ethylene/propylene-butylene-ethylene/propylene)$_n$,
poly(styrene-butylene-ethylene/butylene-butylene-ethylene/butylene)$_n$, poly(styrene-butylene-
ethylene/butylene-butylene-ethylene/propylene)$_n$, poly(styrene-ethylene-ethylene/butylene-butylene-
ethylene/propylene)$_n$, poly(styrene-ethylene-ethylene/propylene-butylene-ethylene/butylene)$_n$,
poly(styrene-ethylene-ethylene/propylene-ethylene-ethylene/propylene-ethylene)$_n$, poly(styrene-
butylene-ethylene/propylene-butylene-ethylene/propylene-butylene)$_n$, poly(styrene-ethylene-
ethylene/propylene-ethylene-ethylene/butylene)$_n$, poly(styrene-ethylene-ethylene/propylene-ethylene-
ethylene/propylene-ethylene/butylene)$_n$, poly(styrene-ethylene-ethylene/propylene-ethylene-
ethylene/propylene-ethylene)$_n$, poly(styrene-ethylene-ethylene/propylene-ethylene/butylene-
ethylene/propylene-ethylene/butylene butylene)$_n$ or a mixture thereof. The G_n can also be made with or
without a (IV) selected amount of at least one polar polymer selected from the group consisting of
ethylene-butyl acrylate, ethylene-ethyl acrylate, ethylene-methyl acrylate, ethylene-vinyl acetate,
ethylene-vinyl acrylate, ethylene-vinyl alcohol, acrylonitrile-styrene-acrylate, styrene-
acrylonitrile, styrene-maleic anhydride, meleated poly(styrene-ethylene-propylene-styrene) or
meleated poly(styrene-ethylene-butylene-styrene); and in combination with or without a (V) selected
amount of at least one crystalline or non-crystalline polymer or copolymer selected from the group
consisting of poly(styrene-butadiene-styrene), poly(styrene-butadiene), poly(styrene-
isoprene-styrene), poly(styrene-isoprene), poly(styrene-ethylene- propylene), low viscosity
poly(styrene-ethylene-propylene-styrene), low viscosity poly(styrene-ethylene-butylene-styrene),
poly(styrene- ethylene-butylene), meleated poly(styrene-ethylene-butylene-styrene), high vinyl
content poly(styrene-ethylene-butylene-styrene), poly(styrene-ethylene-propylene-styrene-ethylene-
propylene), poly(ethylene-propylene), poly(styrene-butadiene)$_n$, poly(styrene-butadiene)n,
poly(styrene-isoprene)$_n$, poly(styrene-isoprene)$_n$, poly(styrene-ethylene-propylene)$_n$, low viscosity
poly(styrene-ethylene-propylene)$_n$, low viscosity poly(styrene-ethylene-butylene)$_n$,
poly(styrene-ethylene-butylene)$_n$, meleated poly(styrene-ethylene-butylene)$_n$, high vinyl content
poly(styrene-ethylene-butylene)$_n$, poly(styrene-ethylene-propylene-styrene-ethylene-propylene)$_n$,
poly(ethylene-propylene)$_n$, polystyrene, polybutylene, poly(ethylene-propylene),
poly(ethylene-butylene), polypropylene, polyethylene, or polypthalamide, wherein said selected block
copolymer is a linear, branched, multiarm, or star shaped copolymer.

As used herein, the term "gel rigidity" in gram Bloom is determined by the gram weight
required to depress a gel a distance of 4 mm with a piston having a cross-sectional area of 1 square
centimeter at 23°C.

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It is found that ● the block copolymer gels described ● n, including insulating gels, insulating gel composites, and fluffy gels, the tensile strength and tear strength are esentially independent properties. For any particular gel, it can exhibit high tensile strength, but weak tear strength. Likewise, a gel can exhibit high tear strength, but low tensil strength. The best tensile and tear strength gels are those having greater crystallinity and elasticity. The tensile of all block copolymer gels including the crystalline gels can be improved by the addition of (1-15% weight) crystalline and seim-crystalline (V) polymers, such as additions of higher density and higher molecular weight (higher melt index) polyethylene and polypropylene. The tear strength can be improved by additions (1-15% weight) of branched, multiblock, radial, star block copolymers (with at least 20% weight end block content), polyethylene copolymers, polypropylene copolymers, thermoplastic polyurethane elastomers, polyphenylene oxide, high molecular weight polystyrene, polycarbonate, and the like. Hence, for example 1-10% weight of polypropylene and 1-10% weight of poly(dimethylphenylene)oxide can further improve the tensile and tear strength of the gels of the invention. Likewise combinations of the other polymers described can provide a balanced of better tensile, better tear and better fatigue resistant gel properties. The higher tensile and tear properties can be compared to that of a Kraton G1651 or SEPTON 8006 (SEBS) and Kraton GRP 6918 or SEPTON 2006 (SEPS) gels having the same rubber to plasticizer ratio, but without the substantial block copolymer crystallinity and tensile and tear improving polymer components. In all cases, the pure (SEBS) and (SEPS) gels exhibit lower tensile, lower tear, and lower fatigue properties.

The various types of high viscosity linear, branched, multiarm, or star shaped block copolymers employed as one or more component(s) forming the insulating gels, G_n as well as the gel component for the fluffy, strong, solid shape recoverable elastic gelatinous elastomer composition, $(G_n M_m)$, of the invention are of the general configurations A-Z-A and $(A-Z)_n$, wherein the subscript n is two or more (e.g., 2, 3, 4, 5, 6, 7, 8, 9, 10, etc). In the case of multiarm block copolymers where n is 2, the block copolymer denoted by $(A-Z)_n$ is the linear block copolymer A-Z-A, for sake of simplicity the stable coupling agent residue is ignored.

The end block segment (A) comprises a glassy amorphous polymer end block segment, preferably, polystyrene and the midblocks (Z) comprises a midblock of poly(ethylene), poly(butylene), poly(ethylene-butylene), poly(ethylene-propylene) or a combination thereof.

Advantageously, G_n can be made substantially more tear resistant, more resistant to high shear and high stress rupturing by selecting block copolymers with one or more substantially crystalline poly(ethylene) midblock (simply denoted by "-E- or (E)") in combination with one or more amorphous midblocks of poly(butylene), poly(ethylene-butylene), poly(ethylene-propylene) or combination thereof (the amorphous midblocks are denoted by "-B- or (B)", "-EB- or (EB)", and "-EP- or (EP)" respectively or simply denoted by "-W- or (W)" (when referring to one or more of the amorphous midblocks as a group) not to be confused with (Z) which denotes the midblocks (-E-, -EB-, -B-, -EP- and -W-) between the end (A) blocks. The A and Z portions are incompatible and form a two or more-phase system consisting of sub-micron amorphous glassy domains (A) interconnected by (Z) chains. The glassy domains serve to crosslink and reinforce the structure. This physical elastomeric network structure is reversible, and heating the polymer above the softening point of the glassy domains temporarily disrupt the structure, which can be restored by lowering the

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temperature.

The G_n of the invention having one or more block copolymers with substantially crystalline polyethylene midblocks are hereafter referred to as "fluffy elastic-crystalline gels" or simpler "fluffy crystal gels". The block midblocks of copolymers forming the fluffy crystal gels are characterized by sufficient crystallinity as to exhibit a melting endotherm of at least about 40°C as determined by DSC curve. The fluffy, elastic solid gelatinous elastomer composition of the invention made from block copolymers having substantially no crystalline polyethylene midblocks are hereafter referred to as "fluffy elastic-amorphous gels" or simpler "fluffy amorphous gels". For simplicity, the fluffy amorphous gels and fluffy crystal gels will be referred to generally as "fluffy gels" or even more simply as G_n above. When referring to the gels' amorphous or crystal nature, they will be referred to as fluffy amorphous gels and fluffy crystal gels.

More surprisingly and advantageously, certain selected unique fluffy crystal gels of the invention have the unique ability to exhibit time delay complete elastic-recovery from its extended or deformed state or shape back to its original state and shape. This is attributed the block copolymer component(s) having a higher crystalline -E- segment midblock(s).

The amorphous block copolymer components are advantageously modified by the presence of the higher crystalline -E- segment(s) which may resist crazing and cavitation that immediately precedes fibrillation of the polystyrene domains due to applied stress causing catastrophic crack development and failure of the fluffy gels without adequate crystalline -E- segments.

The fluffy gels can be made in combination with a selected amount of one or more (IV) and/or (V) polymers and copolymers including thermoplastic crystalline polyurethane elastomers with hydrocarbon blocks, homopolymers, copolymers, block copolymers, polyethylene copolymers, polypropylene, polypropylene copolymers, and the like described below.

The high viscosity linear (I) block copolymers are characterized as having a Brookfield Viscosity value at 5 weight percent solids solution in toluene at 30°C of from at least about 35 cps to about 60 cps and higher, advantageously from about 40 cps to about 160 cps and higher, more advantageously from about 50 cps to about 180 cps and higher, still more advantageously from about 70 cps to about 210 cps and higher, and even more advantageously from about 90 cps to about 380 cps and higher.

The high viscosity (I) branched, star-shaped or multiarm block copolymers are characterized as having a Brookfield Viscosity value at 5 weight percent solids solution in toluene at 30°C of from about 80 cps to about 380 cps and higher, advantageously from about 150 cps to about 260 cps and higher, more advantageously from about 200 cps to about 580 cps and higher, and still more advantageously from about 100 cps to about 800 cps and higher.

The high viscosity linear (I) high vinyl content
SEBS block copolymers are characterized as having a Brookfield Viscosity value at 10 weight percent solids solution in toluene at 25°C of from at least about 35 cps to about 100 cps and higher, advantageously from about 40 cps to about 80 cps and higher, more advantageously from about 50 cps to about 70 cps and higher, still more advantageously from about 50 cps to about 90 cps and higher, and even more advantageously from about 60 cps to about 100 cps and higher.

Using Toluene Viscosity at 10% solids at 25°C of approximately 1,800 cP or the equivalent viscosity at 5 weight percent solids solution in toluene at 30°C of approximate 40 as reference for

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the linear block copolym⬛BS (Kraton G 1651), the various ra⬛considered as high viscosities denoted above for the different block copolymers (linear, multiarm, radial, an branched block copolymers) although somewhat different are substantially comparable in molecular weights.

The various aspects and advantages of the invention will become apparent to those skilled in the art upon consideration of the accompanying disclosure and the drawings.

Extremely Light fluffy, strong, and highly elastic gel compositions are unknown in the art. The solid elastic fluffy gels employed in the present invention are different and not the same as the visco-elastic fluids or materials of patents '913 and '657. The gels of the instant invention do not exhibit the property of visco-elastic fluids and are not flowable in the ambient state, but remains substantially a elastic solid below its "A" domain's glassy disassociation temperature or melting point. In order to make strong, dimensionally stable, solid elastic oil-gels from high viscosity block copolymers, it is necessary to process the oil and high viscosity block copolymers at high temperatures above about 150°C to about 200°C for sufficient long times until a homogeneous molten blend is obtained. Such oil-gels can also be made using high intensity mixers for about 50 minutes at 190°C-210°C under vacuum. Under such process conditions, the molten oil and block copolymer gel viscosities can be quite high depending on the rate of shear. At even low shear rates, the molten block copolymer gel exhibit viscosities greatest at above about the glassy domain melting point. Even above the glassy domain melting point, the melt viscosities can be very high. As an example, the viscosity at 5% concentration in oil at 300°F for a high viscosity poly(styrene-ethylene-butylene-styrene) block copolymer can be as high as 42,700 cps. At about slightly below the processing temperature, the molten high viscosity block copolymer gel becomes a weak solid. At about 300°F, the gel exhibit the character of a weak elastic solid. Of course, at ambient temperature, it is impossible to even incorporate a single microsphere into the gel, because the gel is solid. Consequently, incorporating even a small or moderate amount of microspheres into the molten gel at processing temperatures is difficult. It would only further greatly increase the molten gel's viscosity making it more difficult to process. The increase viscosity with each addition of microspheres makes for an impossible task to obtain a truly light weight fluffy elastic gel. Microspheres such as those made from methacrylonitrile can be easily and quickly destroyed under such long times at high process temperatures and shear above its rupture temperature T_{max}. Incorporation of sufficient amount of methacrylobitrile microspheres to make a light fluffy "closed cell" elastic solid gel is heretofore unrealized and unobtainable. Incorporation of even a small amounts of unexpanded methacrylonitrile microspheres is impossible due to the high molten gel viscosity and temperature conditions. Upon exposure of the unexpanded microspheres to such high process temperature, the microspheres instantly expands and became even more difficult to work into the molten gel due to the microsphere's increased size, low density in combination with the extreme high molten gel viscosity and high process temperatures.

Consequently, adding unexpanded thermoplastic microspheres such as methacrylonitrile microspheres at or near its upper temperature limits T_{max}, will only increase the already high viscosity of the molten oil-block copolymer gel.

The prior art ('657) did not recoGnize the relationship of high temperature, high molten viscosity and high block copolymer concentrations, the prior art would have had no motivation to solve the high molten viscosity problem at the high temperature process conditions; it is apparent

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the prior art avoided the ██ oblem by not adding any microsphere ██ panded or unexpanded) at such high processing temperatures (1) by reducing the block copolymer concentration (thereby lowering the viscosity of the oil and block copolymer composition, and (2) by lowering the temperature of the polymer-oil mixture to ambient before adding any microspheres. Therefore the fluffy gels of the instant invention are not inherent in the process or the composite microsphere and lubricant mixture taught by US patent 5,626,657. Clearly, heating of unexpanded thermoplastic microspheres such as methacrylonitrile microspheres at such high temperatures in a high block copolymer content/oil mixture is not taught by the prior art.

Therefore, a method I found to make a strong, fluffy, elastic solid gel having a density of at least less than 0.6 g/cm^3 is totally unexpected.

Expanded methacrylonitrile microspheres are not advantageous and can not be fully utilized to make the fluffy gels of the invention at the required high process temperatures; while, unexpanded methacrylonitrile microspheres will explode up to almost 50 times their volume (very much like "pop corn") when exposed to above their T_{start} temperatures. The temperature at which they start expanding or popping, however, are too low (106-135°C) to be suitable for incorporation into the high viscosity molten gel at the needed gel processing temperatures. The advantage of using unexpanded microspheres is that they can be very effective for making rapid expansive foams below their T_{max} expansion temperatures provided they do not rupture. Hence, their low T_{max} temperature prevent their use for foaming at the high block copolymer concentrations and high gel processing temperatures. Therefore, the low temperature properties of the unexpanded microspheres and the process conditions of the molten gel makes it impossible to make fluffy gels before the present invention.

The problem is to find ways to enable the unexpanded microspheres to be (i) added and dispersed in substantial quantities in the molten gel without substantially increasing the gel's molten viscosity, (ii) delay or retard the start of their expansion in the molten gel to allow for sufficient dispersion, (iii) limit, restrict or control their exposure the high rupture (T_{max}) temperatures while being dispersed in the molten gel, and (iv) adequately allowing dispersion of the microspheres particles into the molten gel.

Conventionally, in order to lower the molten gel viscosity to provide for sufficient dispersion of the microspheres, the process temperatures needs to be increased which pushes the process temperature even higher above the microsphere's rupture temperature. Whereas, attempting to maintain a sufficient low process temperature (at or below T_{max}) and applying high pressures will require high shear resulting uncontrollable pressure and viscosity fluctuations which will result in inadequate dispersion.

A simple solution to the critical conditions i-iv has been found to provide fluffy gels having a density of at least less than about 0.6 g/cm^3, more advantageously at least about 0.5 g/cm3, still more advantageously at least about 0.4 g/cm3, and still more advantageously at least about 0.3 g/cm3 or less.

Not only are fluffy gels obtained, gels which are fluffy as well as strong, highly elastic, exhibit shape-memory, resistant to tear, high shear and high stress rupturing, and exhibit controlled delay response and slow, complete recovery from extension and deformation are also obtained.

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I have now discov●● a method of incorporating large qu●●ies of unexpanded microspheres, delay the microspheres' onset of expansion by controlling their exposure to high heat, thereby, allowing adequately time to disperse the microspheres particles into the molten gel. The method I found is as follows:

As a first approximation, I determine the time required for adequately mixing a selected volume or mass of molten gel as a function of temperature and molten gel viscosity. This allows for a better understanding of the mixing equipment and conditions chosen for making the fluffy gels of the invention. This can be determined for any large or medium mixing equipment used, even a small test tube.

The components I, II, IV and V of the invention blend easily in the melt and a heated vessel equipped with a stirrer is all that is required. While conventional large vessels with pressure and/or vacuum means can be utilized in forming large batches of the instant fluffy crystal gels in amounts of about 40 lbs or less to 10,000 lbs or more. For example, in a large vessel, inert gases can be employed for removing the composition from a closed vessel at the end of mixing and a partial vacuum can be applied to remove any entrapped bubbles. Stirring rates utilized for large batches can range from about less than 10 rpm to about 40 rpm or higher).

Simply mix a selected, predetermined amount of ingredients I and II in the chosen equipment under heat (at a constant rate of mixing) at the lowest temperature that will provide a homogenous clear, optically transparent molten gel mixture. Add a selected amount of color (e.g., orange color) polypropylene pellets and measure the time required to uniformly disperse the color pellets in the molten gel. Next, increase the temperature to decrease the molten gel viscosity and add a hand full of a different colored high density polypropylene pellets and measure the time required to uniformly dispersed the second colored pellets in the molten gel. Repeat the procedure to obtain a time-temperature-viscosity relationship graph of the time required to uniformly mix a selected volume or mass at increasing temperatures and varying viscosities of the molten gel in the chosen equipment. By this method, the time, t_u, required to uniformly disperse a unite volume or mass in the molten gel at any selected temperature or viscosity can be determined.

In making a fluffy gel, I need to (1) predetermine the rigidity and quantity of the final fluffy gel I wish to make, (2) estimate the final process temperature and viscosity before incorporating the unexpanded microspheres into the hot molten gel, (3) combine selected raw materials (I) and/or (IV) and (V) ingredients, and (4) add a predetermined selected amount of (II) ingredient, (5) blend together the components as desired at about 23°C to about 100°C forming a paste like mixture and further heating said mixture uniformly to about 150°C to about 200°C until a homogeneous molten blend is obtained (Lower and higher temperatures can also be utilized depending on the viscosity of the oils and amounts of block copolymers and polymer used.

With the predetermined amount of the remainder (II) ingredient, I (6) add and mix with it a selected measured quantity of (III) unexpanded microspheres at ambient temperature. The predetermined amount of (II) ingredient utilized initially to make the molten gel can range between less than about 75% to about 95% or higher (according to the criteria set out below). Depending on the final molten gel temperature, viscosity, and volume or quantity of the preselected molten gel, I set the following general guide and requirements: match the viscosity of the mixture of (II) and (III) to form a (IIIa) (unexpanded microsphere/oil) mixture with a viscosity (4b) about as close as

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possible matching the vi⬤ity of the molten gel. I then esti⬤and select a time, t_u, for mixing a unit volume of the molten gel from the graph (temperature, time, viscosity and equipment relationship). Then I determined by measuring in a preheated oven (set at the same temperature as the temperature of the molten gel) the time, t_r, required to raise the temperature of the mass of (IIIa) from ambient to the temperature T_{max}. I then adjust t_r by adding from the remainder ingredient (II) additional amounts to (IIIa) until the time (t_r) equals preferably at least about $1/20(t_u)$, more preferably $1/10(t_u)$, still more preferably about at least $1/4(t_u)$, and especially more preferably about at least $1/2(t_u)$. When the molten gel temperature is below T_{max}, the t_r selected chosen is preferably from about less than $1/10(t_u)$ to about $1/4(t_u)$ or higher. When the molten gel temperature is above t_{max}, the t_r selected is preferably from about less than about $1/4(t_u)$ to about $1/2(t_u)$ or higher. The reason for increasing the mass of IIIa is to prevent the temperature surrounding the microspheres to rise too quickly in the higher temperature molten gel. Hence, the greater the t_u or added mass selected, the lower the viscosity and longer the time available for adequate dispersion of the unexpanded microspheres in the molten gel.

Following the criteria above, a fluffy gel can be obtained of almost any desired density. The polymers forming the gels of the invention are described and illustrate in copending application No. 863,794 and incorporated herein by reference. Theory notwithstanding, the block copolymer structures can be spheroid, cylinders, plates, and ordered bicontinuous are also within the scope of the present invention. Cylinder and plate structure are obtained with increasing glassy A end blocks. From about 15-30% by weight of A blocks, the block copolymer structure is spheroid. From about 30 about 40% by weight of A blocks, the block copolymer structure becomes cylindrical for linear block copolymers and ordered bicontinous structures (OBDD) for multi-arm block copolymers; and above about 45% A blocks, the structure becomes less cylindrical and more plate like for linear block copolymers and about 60% and higher the structure becomes OBDD for linear blocks copolymers as well.

The advantages of sufficient crystalline -E- block copolymer midblock segments for improving gel tear and stress rupturing is unknown in the art. For example, U.S. Patent No. 5,132,355 teaches gelling liquid hydrocarbons by polyethylene block copolymers to yield pumpable hydrocarbon polymer mixtures continuing a gelling polyethylene block copolymer agent. U.S. Patent No. 5,276,100 disclose solid block copolymers having improved resistance to clod flow. Other patents such as U.S. Nos. 5,571,864 and 5,654,364 are directed to miscible polyolefin blends with modifying polyolefin having matching segment lengths and miscible blend of polyolefin and polyolefin block copolymer. These patents are incorporated herein by reference.

Block copolymers containing high butylene midblock segments or substantially equal segment lengths of ethylene and butylene or ethylene and propylene are highly amorphous and are suitable for making fluffy amorphous gels of the invention, but such fluffy gels are generally weaker (with respect to tear, stress, rupture, and fatigue resistance) than crystal gels of the invention.

In order to obtain fluffy elastic crystal gels, however, it is necessary that the selective synthesis of butadiene produce sufficient amounts of 1,4 poly(butadiene) that on hydrogenation can exhibit "crystallinity" in the midblocks. In order for the block copolymers forming the fluffy

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crystal gels of the inve⬤n to exhibit crystallinity, the cry⬤ine midblock segments must contain long runs of $-CH_2-$ groups. There should be approximately at least 16 units of $-(CH_2)-$ in sequence for crystallinity. Only the $(-CH_2-)_4$ units can crystallize, and then only if there are at least 4 units of $(-CH_2-)_4$ in sequence; alternatively, the polyethylene units are denoted by $[-(CH_2-CH_2-CH_2-CH_2)-]_4$, $[(-CH_2-)_4]^4$ or $(-CH_2-)^{16}$. The amount of $(-CH2-)^{16}$ units forming the (E) midblocks of the block copolymers comprising the fluffy crystal gels of the invention should be at least about 20% which amount is capable of exhibiting a melting endotherm in differential scanning calorimeter (DCS) curves.

Advantageously, the elastomer midblock segment should have a crystallinity of at least about 20% of $(-CH_2-)16$ units of the total mole % forming the midblocks of the block copolymer, more advantageously at least about 25%, still more advantageously at least about 30%, especially advantageously at least about 40% and especially more advantageously at least about 50% and higher. Broadly, the crystallinity of the midblocks should range from at least about 20% to about 60%, less broadly from at least about 18% to about 65%, and still less broadly from at least 22% to about 70%.

The melting endotherm in DSC curves of the crystalline block copolymers comprising at least 20% crystallinity are much higher than conventional amorphous block copolymers. The maximum in the endotherm curves of the crystalline block copolymers occurs at about 40°C, but can range from greater than about 25°C to about 60°C and higher. The crystalline block copolymers forming the fluffy crystal gels of the invention can exhibit melting endotherms (as shown by DSC) of about 25°C to about 75°C and higher. More specific melting endotherm values of the crystalline midblock block copolymers include: about 28°C, 29°C, 30°C, 31°C, 32°C, 33°C, 34°C, 35°C, 36°C, 37°C, 38°C, 39°C, 40°C, 41°C, 42°C, 43°C, 44°C, 45°C, 46°C, 47°C, 48°C, 49°C, 50°C, 51°C, 52°C, 53°C, 54°C, 55°C, 56°C, 57°C, 58°C, 59°C, 60°C, 61°C, 62°C, 63°C, 64°C, 65°C, 66°C, 67°C, 68°C, 69°C, 70°C, 71°C, 72°C, 73°C, 74°C, 75°C, 76°C, 77°C, 78°C, 79°C, 80°C, 90°C, 100°C, 110°C, 120°C, and higher, whereas, the melting endotherm (DSC) for conventional amorphous midblock segment block copolymers are about 10°C and lower.

The melting endotherm is seen on heating and a sharp crystallization exotherm is seen on cooling. Such midblock crystallization endothermic and exothermic characteristics are missing from DCS curves of amorphous gels. The crystallization exotherm and fusion endortherm of the crystalline block copolymer gels of the invention are determined by ASTM D 3417 method.

Generally, the method of obtaining long runs of crystalline $-(CH_2)-$ is by sequential block copolymer synthesis followed by hydrogenation. The attainment of fluffy crystal gels of the instant invention is solely due to the selective polymerization of the butadiene monomer (forming the midblocks) resulting in one or more predetermined amount of 1,4 poly(butadine) blocks followed by sequential polymerization of additional midblocks and hydrogenation to produce one or more crystalline midblocks of the final block copolymers.

The crystalline block copolymers are made by sequential block copolymer synthesis, the percentage of crystallinity of $(-CH_2-)^{16}$ units should be at least about $(0.67)^4$ or about 20% and actual crystallinity of about 12%. For example, a selectively synthesized $S-EB_n-S$ copolymer having a ratio of 33:67 of 1,2 and 1,4 poly(butadiene) on hydrogenation will result in a midblock with a crystallinity of $(0.67)^4$ or 20%. For sake of simplicity, when n is a subscript of $-EB-$, n denotes the

percentage of $(-CH2-)_4$ un⬤ eg, n = 33 or 20% crystallinity wh⬤ is the percentage of $(0.67)^4$ or "$(-CH_2-)_{16}$" units. Thus, when n = 28 or 72% of $(-CH_2-)_4$ units, the % crystallinity is $(0.72)^4$ or 26.87% crystallinity attributed to $(-CH_2-)_{16}$ units, denoted by $-EB_{28}-$. As a matter of convention, and for purposes of this specification involving hydrogenated polybutadiene: the notation $-E-$ denotes at least about 85% of $(-CH_2-)_4$ units. The notation $-B-$ denotes at least about 70% of $[-CH_2-CH(C_2H_5)-]$ units. The notation $-EB-$ denotes between about 15 and 70% $[-CH_2-CH(C_2H_5)-]$ units. The notation $-EB_n-$ denotes n% $[-CH_2-CH(C_2H_5)-]$ units. For hydrogenated polyisoprene: the notation $-EP-$ denotes about at least 90% $[-CH_2-CH(CH_3)-CH_2-CH_2-]$ units.

Likewise, in order to obtain the highly amorphous midblock components such as $-B-$ forming the fluffy amorphous gels, it is necessary that the selective synthesis of butadiene produce sufficient amounts of vinyl or 1,2 poly(butadiene) that on hydrogenation can exhibit "substantially amorphous polybutene" midblocks. The notation $-B-$ denotes greater than above about 70% $[-CH2-CH(C2H5)-]n$ polybutene units and $-P-$ denotes greater than about about 70% $[-CH(CH-2CH3)-CH2-]_n$ polyisopropylethyene units. The substantially amorphous midblocks $-EB_n-$ and $-EP_n-$ of SEB_nS and SEP_nS (or more simply denoted when n% is greater than about 70% as $-B-$ and $-P-$) are more advantageously when n% is greater than about 75%, still more advantageously greater than about 80%, and still more advantageously greater than about 85%, and even still more advantageously greater than about 90% or higher. Typically, high polybutene content SEB_nS or simply SBS is made by adding structure modifiers, such as ethers, which gives more 1,2 polybutadiene and after hydrogenation, more polybutene, resulting in less crystallinity, softer block copolymer, lower viscosity, and higher Tg. Likewise, high polyisopropylethyene content SEP_nS or simply S-P-S is made by adding structure modifiers to give more 3,4 structure and after hydrogenation, more polyisopropylethyene, resulting in softer block copolymer, lower viscosity, and higher Tg.

The major advantages of SEB_nS and SEP_nS over SEBS, SEPS (when n% = greater than about 70%) is the Tg of poly(styrene-ethylene-butylene>70-styrene) and poly(styrene-ethylene/propyene-isopropylethyene>70-styrene) are much higher; the gel rigidities are lower; and the viscosities are much lower. More specifically, the Tg of SEBS is typically about $-58°C$ and the Tg of SEPS is typically about -50 to about -60 °C. Whereas, the Tg of SEB_nS and SEP_nS with high butylene content and high isopropylethyene content can be advantageously much higher of about less than about $-40°C$, advantageously $-30°C$ and more advantageously higher of about -27 °C and higher.

It is extraordinary that where typical SEBS and SEPS fluffy amorphous gels fails to provide greater tensile strength, fails to provide greater tear strength, and fails to provide greater resistance to high stress rupture, hereto unknown and unappreciated modification of the midblock structures provide heretofore unrealizable improved higher tensile strength, improved higher tear strength, and improved higher resistance to high stress rupture.

Theory notwithstanding, SEBS and SEPS or fluffy amorphous gels fail to provide greater improved properties. The following is known:

i) fluffy amorphous gels made from typical SEBS which is created from a mixture of 1, 4- and 1,2-polybutadiene to provide a random mixture of ethylene and butylene units greater to suppress

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crystallinity (as noted █████gge). Such fluffy amorphous gels c█████t provide greater tear strength and lack greater resistance to high stress rupture.

ii) fluffy amorphous gels made from typical SEPS which is created by hydrogenation of cis-1,4-polyisoprene results in a 1:1 ethylene/propylene elastomer midblock (as noted by Legge). Such fluffy amorphous gels can not provide greater tear strength and lack greater resistance to high stress rupture.

Contrary to the inferior properties of the above fluffy amorphous gels 1) and 2), the following fluffy crystal gels are found to be superior and of improved high tear strength, improved resistance to high stress rupture and sufficient greater tensile strength:

iii) fluffy crystal gels made from an admixture of a high crystalline ethylene content $S-E_nB-S$ block copolymer and a high butylene content $S-EB_n-S$ block copolymer.

iv) fluffy crystal gels made from an admixture of a high crystalline ethylene content $S-E_nB-S$ block copolymer and a high polyisopropylethyene content $S-EP_n-S$ block copolymer.

v) fluffy crystal gels made from an admixture of a high crystalline ethylene content $S-E_nB-S$ block copolymer, a high butylene content $S-EB_n-S$ block copolymer, and a high polyisopropylethyene content $S-EP_n-S$ block copolymer

vi) $S-E-EB_{>70}-E-S$ fluffy crystal gels made by coupling $S-E-EB_{>70}$.

vii) $S-E-EP_{>70}-E-S$ fluffy crystal gels made by coupling $S-E-EP_{>70}$.

viii) fluffy crystal gels made from linear, branched, radial, star-shaped, multi-arm or branched block copolymers having sufficient multiple midblock components of high crystalline ethylene content, high butylene content, and/or high isopropylethyene content including all combinations, sequential additions and permutations and mixtures of such block copolymers and as described herein are of the greatest advantage.

Generally, one or more (E) midblocks can be incorporated at various positions along the midblocks of the block copolymers. Using the sequential process for block copolymer synthesis, The (E) midblocks can be positioned as follows:

i)	A-E-W-A	ii)	A-E-W-E-A
ii)	A-W-E-W-A	iii)	A-E-W-E-W-E-W-E-A
iv)	A-W-E-W-A-E-A-E-W-E-A	v)	A-W-A
vi)	A-E-A, etc.		

The lower flexibility of the block copolymer fluffy crystal gels due to high (E) content midblocks can be balanced by the addition of sequentially formed (W) midblocks. For example, the sequentially synthesized block copolymer S-E-EB-S can maintain a high degree of flexibility due to the presence of amorphous -EB- block. The sequential block copolymer S-E-EB-B-S can maintain a high degree of flexibility due to the presence of amorphous -EB- and -B- midblocks. The sequential block copolymer S-E-EP-E-S can maintain a high degree of flexibility due to the presence of -EP- midblock. The sequential block copolymer S-E-B-S can maintain a high degree of flexibility due to the presence of the -B- midblock. For S-E-S, where the midblock is substantially crystalline and flexibility low, physical blending with amorphous block copolymers such as S-EB-S, S-B-S, S-EP-S, S-EB-EP-S, $(S-EP)_n$ and the like can produce more softer, less rigid, and more flexible fluffy crystal gel.

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In additional to ⬤lock copolymers S-E-EB-S and S-E-E⬤ such other block copolymers such as, for example, S-E-EB-E-S can be made by coupling S-E-EB and S-E-EP-E-S can be made by coupling S-E-EP or by making it sequentially. Multi-arm of such block copolymers can also be made.

Because of the (E) midblocks, the fluffy crystal gels of the invention exhibit different physical characteristics and improvements over substantially amorphous gels including damage tolerance, improved crack propagation resistance, improved tear resistance producing knotty tears as opposed to smooth tears, crystalline melting point of at least 28°C, improved resistance to fatigue, higher hysteresis, etc. Moreover, the fluffy crystal gels when stretched exhibit additional yielding as shown by necking caused by stress induced crystallinity. Additionally, the crystallization rates of the crystalline midblocks can be controlled and slowed depending on thermal history producing time delay recovery upon deformation. Gels exhibiting time delay recovery following deformation is of great advantage and an improvement over fluffy amorphous gels and fluffy crystal gels for certain uses.

Gels having such time delay recovery properties are unique. Such gels of the invention can achieve delay times of from about less than 2 seconds to about 20 seconds or more. Characteristic delay times that can be achieved are from about 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24, 25, 26, 27, 28, 29, 30, 40, 50, 60, 70, 80, 90, 100, 120, seconds and longer. Consequentially, the recovery characteristics of the time delay fluffy gels are due to the stress induced crystallization of the block copolymers used.

Surprisingly, linear, multiarm, radial, or branched block copolymers when formed into gels which exhibit such time delay behavior always have crystalline -E- component in their midblocks and are characterized as having a Brookfield Viscosity value at 5 weight percent solids solution in toluene at 30°C of from about 120 cps to about 350 cps and higher, advantageously from about 130 cps to about 260 cps and higher, more advantageously from about 180 cps to about 380 cps and higher, and still more advantageously from about 200 cps to about 800 cps and higher. Additionally, the onset of this strange behavior is observed after the molten gel is allowed to remained undisturbed or unstirred for a selected amount of time before forming into shaped articles. It appears that crystallinity, extreme viscosities, cooling, heating and/or shear histories of the molten gels affects the onset of the time delay behavior of the room temperature gels.

Regarding the great advantage of the fluffy crystal gels' resistance to fatigue, fatigue (as used herein) is the decay of mechanical properties after repeated application of stress and strain. Fatigue tests give information about the ability of a material to resist the development of cracks or crazes resulting from a large number of deformation cycles. Fatigue test can be conducted by subjecting samples of fluffy amorphous and crystal gels to deformation cycles to failure (appearance of cracks, crazes, rips or tears in the gels).

Tensile strength can be determined by extending a selected gel sample to break as measured at 180° U bend around a 5.0 mm mandrel attached to a spring scale. Likewise, tear strength of a notched sample can be determined by propagating a tear as measured at 180° U bend around a 5.0 mm diameter mandrel attached to a spring scale.

Various block copolymers can be obtained which are amorphous, highly rubbery, and exhibiting minimum dynamic hysteresis:

The block copolymer of (A-Z-A) can be obtained by sequential synthesis methods followed by hydrogenation of the midblocks. As denoted above, abbreviations are interchangeably used, for example, (S-E-EP-S) denotes poly(styrene-ethylene-ethylene-co-propylene-styrene). Other linear block copolymers (denoted in abbreviations) include the following: (S-E-S), (S-Butylene-S), (S-E-EB-S), (S-E-EP-S), (S-B-EP-S), (S-B-EB-S), (S-E-EP-E-S), (S-E-EB-B-S), (S-B-EP-B-S), (S-B-EB-B-S), (S-E-B-EB-S), (S-E-B-EP-S), (S-EB-EP-S), (S-E-EB-EP-S), (S-E-EP-EB-S), (S-B-EB-EP-S), (S-B-EP-EB-S), (S-E-EP-E-EP-S), (S-E-EP-E-EB-S), (S-EP-B-EP-S), (S-B-EB-B-EB-S), (S-B-EB-B-EP-S), (S-E-EB-B-EP-S), (S-E-EP-B-EB-S), (S-E-EP-E-EP-E-S), (S-B-EP-B-EP-B-S), (S-E-EP-E-EB-S), (S-E-EP-E-EP-EB-S), (S-E-EP-E-EP-E-S), (S-E-EP-EB-EP-EB-B-S), (S-E-EP-EB-EP-EB... . -S) and the like.

The multiblock star-shaped (or radial) copolymers (A-Z)$_n$X can be obtained by sequential synthesis methods including hydrogenation of selected block copolymers made by polymerizing half of the block copolymers such as SBS or SIS and couple the halves with a coupling agent such as an organic dihalide; or couple with an agent such as SnCl4, which results in star-shaped block copolymers (four branches). Coupling with divinyl benzene give block copolymers which are very highly branched. Radial block copolymers suitable for use in forming the fluffy crystal gels of the present invention include: (S-E)$_n$, (S-E-EB)$_n$, (S-E-EP)$_n$, (S-B-EP)$_n$, (S-B-EB)$_n$, (S-E-EP-E)$_n$, (S-E-EB-B)$_n$, (S-B-EP-B)$_n$, (S-B-EB-B)$_n$, (S-E-B-EB)$_n$, (S-E-B-EP)$_n$, (S-EB-EP)$_n$, (S-E-EB-EP)$_n$, (S-E-EP-EB)$_n$, (S-B-EB-EP)$_n$, (S-B-EP-EB)$_n$, (S-E-EP-E-EP)$_n$, (S-E-EP-E-EB)$_n$, (S-EP-B-EP)$_n$, (S-B-EB-B-EB)$_n$, (S-B-EB-B-EP)$_n$, (S-E-EB-B-EP)$_n$, (S-E-EP-B-EB)$_n$, (S-E-EP-E-EP-E)$_n$, (S-B-EP-B-EP-B)$_n$, (S-E-EP-E-EB)$_n$, (S-E-EP-E-EP-EB)$_n$, (S-E-EP-E-EP-E)$_n$, (S-E-EP-EB-EP-EB-B)$_n$ and counter part multifunctional block copolymers:(R)$_n$-E-S, (R)$_n$-E-EB-S, (R)$_n$-E-EP-S, (R)$_n$-E-EP-E-S, (R)$_n$-E-EB-B-S, (R)$_n$-E-B-EB-S, (R)$_n$-E-B-EP-S, (R)$_n$-E-EB-EP-S, (R)$_n$-E-EP-EB-S, (R)$_n$-E-EP-E-EP-S, (R)$_n$-E-EP-E-EB-S, (R)$_n$-E-EB-B-EP-S, (R)$_n$-E-EP-B-EB-S, (R)$_n$-E-EP-E-EP-E-S, (R)$_n$-E-EP-E-EB-S, (R)$_n$-E-EP-E-EP-EB-S, (R)$_n$-E-EP-E-EP-E-S, (R)$_n$-E-EP-EB-EP-EB-B-S, (R)$_n$-E-EP-EB-EP-EB..... -S, and the like. In the above notation, "-E-" denotes substantially crystalline polyethylene midblock.

The selected amount of crystallinity in the midblock should be sufficient to achieve improvements in one or more physical properties including improved damage tolerance, improved crack propagation resistance, improved tear resistance, improved resistance to fatigue of the bulk gel and resistance to catastrophic fatigue failure of fluffy crystal gel composites, such as between the surfaces of the fluffy crystal gel and substrate or at the interfaces of the interlocking material(s) and fluffy crystal gel, which improvements are not found in amorphous gels at corresponding gel rigidities.

Selected linear block and radial copolymers utilized in forming the fluffy crystal gels of the invention are characterized as having an ethylene to butylene midblock ratio (E:B), an ethylene to ethylene/propylene (E:EP) ratio, and an ethylene to ethylene/butylene (E:EB) ratio of about 85:15 to about 65:35. Advantageously, the butylene concentration of the midblock is about 35% or less, more advantageously, about 30% or less, still more advantageously, about 25% or less, especially advantageously, about 20% or less. Advantageously, the ethylene to butylene midblock ratios can range from about 89:11, 88:12, 87:13, 86:14, 85:15, 84:16, 83:17, 82:18, 81:19, 80:20, 79:21, 78:22, 77:23, 76:24, 75:25, 74:26, 73:27, 72:28, 71:29, 70:30, 69:31, 68:32, 67:33, 66:34 to about 65:35.

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The A to Z midblock ratio of the block copolymers suitable for forming fluffy crystal gels of the invention can range from about 20:80 to 40:60 and higher. More specifically, the values can be 15:85, 19:81, 20:80, 21:79. 22:78. 23:77, 24:76, 25:75, 26:74, 27:73, 28:72, 29:71, 30:70, 31:69, 32:68, 33:67, 34:66, 35:65, 36:64, 37:63, 38:62, 39:61, 40:60, 41:59, 42:58, 43:57, 44:65, 45:55, 46:54, 47:53, 48:52, 49:51, 50:50, 51:49 and 52:48.

As described above, the G_n can also be made with or without a (IV) selected minor amount (from about less than 0.5% to about 10% or more) of at least one polar polymer components such as copolymer selected from the group consisting of ethylene-butyl acrylate, ethylene-ethyl acrylate, ethylene-methyl acrylate, ethylene-vinyl acetate, ethylene-vinyl acrylate, ethylene-vinyl alcohol, acrylonitrile-styrene-acrylate, styrene-acrylonitrile, styrene-maleic anhydride, meleated poly(styrene-ethylene-propylene-styrene) or meleated poly(styrene-ethylene-butylene-styrene) and the like. Such polar components are more compatible with the polar thermoplastic microspheres as well as co-compatibly with the non-polar components of the block copolymers forming the fluffy gels of the invention. Such polar additives can counteract to some degree the lowering of the physical properties due to increasing amounts of microsphere needed to achieve lower densities of the fluffy gels.

The insulating gels and extraordinary fluffy gels can comprise selected major or minor amounts of one or more additional crystalline or non-crystalline polymers or copolymers (V) described above, provided the amounts and combinations are selected do not substantially decreasing the desired.properties. Such V components also include polyethyleneoxide (EO), poly(dimethylphenylene oxide), teflon, optical clear amorphous copolymers based on 2,2-bistrifluoromethyl-4,5-difuoro-1,3-dioxole (PDD) and tetrafluoroethylene (TFE) and the like. Still, other (V) polymers include homopolymers which can be utilized in minor amounts; these include: polystyrene, polydimethylsiloxane, polyolefins such as polybutylene, polyethylene, polyethylene copolymers, polypropylene (such as Dow polypropylene homopolymers H700-12, 700-12A, 700-12NA, 701-20, 702-35, 704, 705, 103-00, 303-02, 500-35, 501, 104, 505; polypropylene copolymers C101-00, C102-04, C103-04, C707-12, C707-12U, C702-20, C708-21U, C709-30, C700-35N, C703-35U, and the like. Polyurethane elastomers based on saturated hydrocarbon diols (Handlin, D., Chin. S., and Masse. M., et al. "POLYURETHANE ELASTOMERS BASED ON NEW SATURATED HYDROCARBON DIOLS" Published Society of Plastics Industry, Polyurethane Division, Las Vegas, October 23, 1996) are also suitable for use in blending with the block copolymers (I) used in forming the gels or fluffy crystal gels of the invention. Such saturated hydrocarbon diols include hydroxyl terminated oligomers of poly(ethylene-butylene) (EB), poly(ethylene-propylene) (EP), -E-EB-, -E-EP-, -B-EP-, -B-EB-, -E-EP-E-, -E-EB-B-, -B-EP-B-, -B-EB-B-, -E-B-EB-, -E-B-EP-, -EB-EP-, -E-EB-EP-, -E-EP-EB-, -B-EB-EP-, -B-EP-EB-, -E-EP-E-EP-, -E-EP-E-EB-, -B-EP-B-EB-, -B-EB-B-EB-, -B-EB-B-EP-, -E-EB-B-EP-, -E-EP-B-EB-, -E-EP-E-EP-E-, -B-EP-B-EP-B-, -E-EP-E-EB-, -E-EB-E-EP-EB-, -E-EP-E-EP-E-, -E-EP-EB-EP-EB-B- and the like. As an example, thermoplastic polyurethane (TPU) made with diisocyanates and chain extenders such as 2,2,4-trimethyl-1,3-pentancdiol (TMPD) and 2-Butyl-2-ethyl-1,3-pentanediol (BEPD) from saturated hydrocarbon diol KLP L-2203 having a hard segment contents of 22% exhibits clean phase separation of the hard and soft segments with a glass transition of -50°C. TPU polyurethane elastomers based on KLP L-2203 diol, MDI with TMPM and BEPD chain extenders at 22% hard segment, 104 isocyanate index, and cured at 105°C gives 2,430 and 1,160 tensile psi, 1040% and 2180% elongation at break, and

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modulus at 300% elongati⬤ 670 and 290 psi respectively by t⬤e shot method. Polyurethane elastomers prepared by the one shot method based on KLP L-2203, MDI and TMP at 1.04 NCO/OH ratio having hard segment concentrations of 22%, 33% and 44% give tensile of 2430, 2830 and 2760 psi respectively, elongations at break of 1040%, 830%, and 760% respectively, and modulus at 300% elongation of 670, 1160 and 1360 psi respectively. KLP L-2203 (hydroxyl terminated poly(ethylene-butylene) oligomer (50,000 cps at 20°C) based TPU's can be mixed with the crystalline block copolymers to form soft fluffy crystal gels within the gel rigidity ranges of the invention. The thermoplastic crystalline triblock and multiblock polyurethane elastomers can also be blended by themselves with components II and III to make strong, elastic fluffy gels of the invention. Hence, thermoplastic polyurethanes with hard segment contents of form about less than 22% to about 45% and higher are of great advantage in forming the fluffy gels of the invention.

Suitable V components for use in the present invention include polyolefins (polyethylene and polyethylene copolymers), such as Dow Chemical Company's Dowlex 3010, 2021D, 2038, 2042A, 2049, 2049A, 2071, 2077, 2244A, 2267A; Dow Affinity ethylene alpha-olefin resin PL-1840, SE-1400, SM-1300; more suitably: Dow Elite 5100, 5110, 5200, 5400, Primacor 141--XT, 1430, 1420, 1320, 3330, 3150, 2912, 3340, 3460; Dow Attane (ultra low density ethylene-octene-1 copolymers) 4803, 4801, 4602 and the like. Polyolefins such as these (in minor amounts) can improve the tear and rupture resistance of the compositions of the invention due to their crystalline contributions.

The conventional term "major" means about 51 weight percent and higher (e.g. 51%, 52%, 55%, 60%, 65%, 70%, 75%, 80% and the like) and the term "minor" means 49 weight percent and lower (e.g. 1%, 2%, 5%, 10%, 15%, 20%, 25% and the like).

Additional example of polymers, copolymers, and blends include: (a) Kraton G 1651, G 1654X; (b) Kraton G 4600; (c) Kraton G 4609; other suitable high viscosity polymer and oils include: (d) Tuftec H 1051; (e) Tuftec H 1041; (f) Tuftec H 1052; (g) Kuraray SEPS 4033; (h) Kuraray S-EB-S 8006; (i) Kuraray SEPS 2005; (j) Kuraray SEPS 2006 , and (k) blends (polyblends) of (a)-(h) with other polymers and copolymers include: (1) S-EB-S/SBS; (2) S-EB-S/SIS; (3) S-EB-S/(SEP); (4) S-EB-S/(SEB)$_n$; (5) S-EB-S/(SEB)$_n$; (6) S-EB-S/(SEP)$_n$; (7) S-EB-S/(SI)$_n$; (8) S-EB-S/(SI) multiarm; (9) S-EB-S/(SEB)$_n$; (10) (SEB)$_n$ star-shaped copolymer; (11) s made from blends of (a)-(k) with other homopolymers include: (12) S-EB-S/polystyrene; (13) S-EB-S/polybutylene; (14) S-EB-S/poly-ethylene; (14) S-EB-S/polypropylene; (16) SEP/S-EB-S, (17) SEP/SEPS, (18) SEP/SEPS/SEB, (19), SEPS/S-EB-S/SEP, (20), SEB/S-EB-S (21), EB-EP/S-EB-S (22), S-EB-S/EB (23), S-EB-S/EP (24), (25) (SEB)$_n$ s, (26) (SEP)$_n$, (27) Kuraray 2007 (SEPS), (28) Kuraray 2002 (SEPS), (29) Kuraray 4055 (S-EB-EP-S) (30) Kuraray 4077 (S-EB-EP-S) (31) Kuraray 4045 (S-EB-EP-S) (32) (S-EB-EP)$_n$, (33) (SEB)$_n$, (34) EPDM, (35) EPR, (36) EVA, (37) coPP, (38) EMA, (39) EEA, (40) DuPont Teflon AF amorphous fluoropolymers, (41) Dow polydimethylsiloxane, (42) maleated S-EB-S (maleation level 2-30%), (43) (EP)$_n$, GRP-6918 (SEPS), G1730 (SEPSEP), G1780 (SEP)n, GRP-6906 (SEPS), GRP-6917 (SEBS), KX-219, KX-222, KX-605, RP-6919 (SEBIS) and the like.

Representative examples of commercial elastomers that can be combined with the block copolymers (I) described above include: Shell Kratons D1101, D1102, D1107, D1111, D1112, D1113X, D1114X, D1116, D1117, D1118X, D1122X, D1125X, D1133X, D1135X, D1184, D1188X, D1300X, D1320X, D4122, D4141, D4158, D4240, D1144, D1184, G1650, G1652, G1654, RP6917, G1657, G1701X, G1702X, G1726X,

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G1750X, G1765X, FG1901X, ●21X, D2103, D2109, D2122X, D3202, ●, D3226, D5298, D5999X, D7340, G1650, G1651, G1652, G4609, G4600, G1654X, G2701, G2703, G2705, G1706, G2721X, G7155, G7430, G7450, G7523X, G7528X, G7680, G7705, G7702X, G7720, G7722X, G7820, G7821X, G7827, G7890X, G7940, G1730M, FG1901X and FG1921X. Kuraray's SEP, SEPS, S-EB-S, S-EB-EP-S Nos. 1001, 1050, 2027, 2003, 2006, 2007, 2008, 2023, 2043, 2063, 2050, 2103, 2104, 2105, 4033, 4045, 4055, 4077, 8004, 8006, 8007, H-VS-3 (S-V-EP)n, Kraton G 1901, 1921, 1924 and the like.

The block copolymers can have a broad range of styrene to ethylene-butylene ratios (S:EB) and styrene to ethylene-propylene ratios (S:EP) of about 20:80 or less to about 40:60 or higher. The S:EB weight ratios can range from lower than about 20:80 to above about 40:60 and higher.

The Brookfield Viscosity of a 5 weight percent solids solution in toluene at 30°C of 2006, 4045, 4055, 4077 typically range about 20-35, about 25-150, about 60-150, about 200-400 respectively. Typical Brookfield Viscosities of a 10 weight percent solids solution in toluene at 30°C of 1001, 1050, 2007, 2063, 2043, 4033, 2005, 2006, are about 70, 70, 17, 29, 32, 50, 1200, and 1220 respectively. Typical Brookfield Viscosity of a 25 weight percent solids solution in toluene at 25°C of Kraton D1101, D1116, D1184, D1300X, G1701X, G1702X are about 4000, 9000, 20000, 6000, 50000 and 50000 cps respectively. Typical Brookfield Viscosity of a 10 weight percent solids solution in toluene at 25°C of G1654X is about 370 cps. The Brookfield Viscosities of a 20 and 30 weight percent solids solution in toluene at 30°C of H-VS-3 are about 133 cps and 350 cps respectively.

Suitable block copolymers and their typical viscosities are further described. Shell Technical Bulletin SC:1393-92 gives solution viscosity as measured with a Brookfield model RVT viscometer at 25°C for Kraton G 1654X at 10% weight in toluene of approximately 400 cps and at 15% weight in toluene of approximately 5,600 cps. Shell publication SC:68-79 gives solution viscosity at 25°C for Kraton G 1651 at 20 weight percent in toluene of approximately 2,000 cps. When measured at 5 weight percent solution in toluene at 30°C, the solution viscosity of Kraton G 1651 is about 40. Examples of high viscosity S-EB-S triblock copolymers includes Kuraray's S-EB-S 8006 which exhibits a solution viscosity at 5 weight percent at 30°C of about 51 cps. Kuraray's 2006 SEPS polymer exhibits a viscosity at 20 weight percent solution in toluene at 30°C of about 78,000 cps, at 5 weight percent of about 27 cps, at 10 weight percent of about 1220 cps, and at 20 weight percent 78,000 cps. Kuraray SEPS 2005 polymer exhibits a viscosity at 5 weight percent solution in toluene at 30°C of about 28 cps, at 10 weight percent of about 1200 cps, and at 20 weight percent 76,000 cps. Other grades of S-EB-S, SEPS, (SEB)$_n$, (SEP)$_n$ polymers can also be utilized in the present invention provided such polymers exhibits the required high viscosity. Such S-EB-S polymers include (high viscosity) Kraton G 1855X which has a Specific Gravity of 0.92, Brookfield Viscosity of a 25 weight percent solids solution in toluene at 25°C of about 40,000 cps or about 8,000 to about 20,000 cps at a 20 weight percent solids solution in toluene at 25°C.

The styrene to ethylene and butylene (S:EB) weight ratios for the Shell desiGnated polymers can have a low range of 20:80 or less. Although the typical ratio values for Kraton G 1651, 4600, and 4609 are approximately about 33:67 and for Kraton G 1855X approximately about 27:73, Kraton G 1654X (a lower molecular weight version of Kraton G 1651 with somewhat lower physical properties such as lower solution and melt viscosity) is approximately about 31:69, these ratios can vary broadly from the typical product specification values. In the case of Kuraray's S-EB-S polymer 8006 the S:EB weight ratio is about 35:65. In the case of Kuraray's 2005 (SEPS), and 2006 (SEPS), the

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S:EP weight ratios are 2⬤ and 35:65 respectively. The styren⬤ ethylene-ethylene/propylene (S:EB-EP) ratios of Kuraray's SEPTON 4045, 4055, and 4077 are typically about 37.6, 30, 30 respectively. More typically the (S:EB-EP) and (S:EP) ratios can vary broadly much like S:EB ratios of S-EB-S and $(SEB)_n$ from less than 19:81 to higher than 51:49 (as recited above) are possible. It should be noted that multiblock copolymers including SEPTON 4045, 4055, 4077 and the like are described in my cited copending parent applications and are the subject matter of related inventions.

The block copolymers such as Kraton G 1654X having ratios of 31:69 or higher can be used and do exhibit about the same physical properties in many respects to Kraton G 1651 while Kraton G 1654X with ratios below 31:69 may also be use, but they are less advantageous due to their decrease in the desirable properties of the final gel.

Plasticizers (II) particularly advantageous for use in practicing the present invention are will known in the art, they include rubber processing oils such as paraffinic and naphthenic petroleum oils, highly refined aromatic-free paraffinic and naphthenic food and technical grade white petroleum mineral oils, and synthetic liquid oligomers of polybutene, polypropene, polyterpene, etc. The synthetic series process oils are high viscosity oligomers which are permanently fluid liquid nonolefins, isoparaffins or paraffins of moderate to high molecular weight.

The amount of plasticizing oil (II) sufficient to achieve gel rigidities of from less than about 2 gram Bloom to about 3,000 gram Bloom range from less than about 250 to about 2,000 parts by weight of a plasticizing oil.

Examples of representative commercially available plasticizing oils include Amoco® polybutenes, hydrogenated polybutenes, polybutenes with epoxide functionality at one end of the polybutene polymer, liquid poly(ethylene/butylene), liquid hetero-telechelic polymers of poly(ethylene-butylene-styrene) with epoxidized polyisoprene and poly(ethylene/butylene) with epoxidized polyisoprene: Example of such polybutenes include: L-14 (320 M_n), L-50 (420 M_n), L-100 (460 M_n), H-15 (560 M_n), H-25 (610 M_n), H-35 (660 M_n), H-50 (750 M_n), H-100 (920 M_n), H-300 (1290 M_n), L-14E (27-37 cst @ 100°F Viscosity), H-300E (635-690 cst @ 210°F Viscosity), Actipol E6 (365 M_n), E16 (973 M_n), E23 (1433 M_n), Kraton KLP L-2203 and Kraton KLP L-1203, EKP-206, EKP-207, HPVM-2203 and the like. Example of various commercially oils include: ARCO Prime (55, 70, 90, 200, 350, 400 and the like), Duraprime and Tufflo oils (6006, 6016, 6016M, 6026, 6036, 6056, 6206, etc), other white mineral oils include: Bayol, Bernol, American, Blandol, Drakeol, Ervol, Gloria, Kaydol, Litetek, Lyondell (Duraprime 55, 70, 90, 200, 350, 400, etc), Marcol, Parol, Peneteck, Primol, Protol, Sontex, Witco brand white oils including RR-654-P and the like. Generally, plasticizing oils with average molecular weights less than about 200 and greater than about 700 may also be used (e.g., H-300 (1290 M_n)).

Comparisons of oil extended S-EB-S triblock copolymers have been described in Shell Chemical Company Technical Bulletin SC:1102-89 (April 1989) "KRATON® THERMOPLASTIC RUBBERS IN OIL GELS" which is incorporated herein by reference.

Of great advantage are the unexpanded particulate materials which can be dispersed and within a controlled temperature heating range can produce a predetermined volume of closed cell particulate dispersions forming the fluffy gels. The particulate materials useful are unexpanded microspheres of

poly(acrylonitrile-metha●nitrile) copolymers encapsulated l●isopentane which are available from Akzo Nobel by the tradename Expancel. The thermoplastic microspheres comprises at least about 80% weight of copolymer and about 6 to about 16% isopentane and are further characterized as having a unexpanded relative density of about 1.2 (H_2O = 1.0), particle size of about 3 to about 50 microns, a T_{start} or softing temperature of about 106°C to about 135°C and a decomposition or rupturing temperature T_{max} of about 138°C to about 195°C. The unexpanded thermoplastic microspheres are activated by heat and expand to approximately about 50 times its unexpanded size to provide an average particle density of about less than 0.020 specific gravity. Their lowest calculated density reached at T_{max} during TMA test is between about 0.25 to about .017 g/cm^3. More specifically, unexpanded grades of microspheres include grades followed by (range of temperatures T_{start}°C/T_{max}°C): #051 (106-111/138-147), #053 (95-102/137-145), #054 (125-135/140/150), #091 (118-126/161-171), #091-80 (118-126/171-181), and #092-120 (118-126/185-195). Other expandable thermoplastic microspheres can be of advantage in making the fluffy gels of the invention. Such should be of higher temperature activated unexpanded thermoplastic microspheres with liquid isopentane, isobutane cores, and the like. Suitably higher T_{start} and T_{max} temperature unexpanded thermoplastic microspheres contemplated for use in the present invention can have (T_{start}/T_{max}) of about (110°C/200°C), (100°C/205°C), (100°C/210°C), (100°C/215°C), (100°C/220°C). (100°C/225°C), (100°C/230°C), (100°C/235°C) and higher.

Fluffy gels of the invention of densities of about 0.6 g/cm^3 comprises about at least above about 5% - 6% by weight of unexpanded microspheres, at about 0.5 g/cm^3, the amount of microspheres is approximately about 10% - 11% by weight, at about 0.4 g/cm^3, the amount of microspheres is about 12% - 15%, and at about 0.3 g/cm^3, the amount of microspheres is about 18% - 20% or higher. Higher density gels (about 0.7 g/cm^3 and about 0.8 g/cm^3) can also be made following the teachings of the present invention. Suitable amounts of unexpanded microspheres useful in forming the fluffy gels of the invention can range from about less than 5% to 30% or higher, more suitably, from about 5% to 25% or higher, and still more suitably, from about 5% to about 20% or higher. As the densities of the fluffy gels of the invention is made less and less, the physical properties of the fluffy gels also are more and more affected. The fluffy crystal gel physical properties remain substantially higher than the physical properties of the fluffy amorphous gels of the invention. This is due to the crystalline contributions as described earlier.

Microspheres incapable of softing by heat and therefore are unexpandable or remains unexpanded, such as phenolic microspheres are not suitable for making the fluffy gels of the present invention because phenolic, a heat-cured thermoset, is the reaction product of phenol and formaldehyde and the structured formed gives it heat resistance, dimensional stability, creep resistance and hardness. Likewise glass microspheres, metal, quartz and carbon microspheres and the like are not suitable for use in making gels having high concentration of microspheres. Such microspheres, however, are suitable for making gels having low concentration of microspheres.

Accordingly, a selected amount of one or more of the heat activated unexpanded thermoplastic particulate materials are dispersed in an ordered, random, homogeneous, nonhomogeneous, stratified, partially stratified or one or more separated phases. The dispersed unexpanded particulate materials are capable of producing a predetermined volume of closed cell particulate dispersion forming the fluffy gels with densities of at least less than about 0.60 g/cm3. The fluffy gels further having a

gel rigidity of from abo██ to about 3,000 gram Bloom, and an ██gation of at least 200%. Typical densities which can be achieved can range from greater than about 0.6 g/cm3 to less that about 0.3 g/cm3. Fluffy gel densities of about 0.75, 0.70, 0.65, 0.60, 0.55, 0.50, 0.45, 0.40, 0.35, 0.30 or lower can be achieved using the unexpanded particulate materials.

The fluffy gels can be made non-adhearing, non-sticking, (non-tacky), by incorporating an advantage amount of stearic acid (octadecanoic acid), metal stearates (e.g., calcium stearate, maGnesium stearate, zinc stearate, etc.), polyethylene glycol distearate, polypropylene glycol ester or fatty acid, and polytetramethylene oxide glycol disterate, waxes, stearic acid and waxes, metal stearate and waxes, metal stearate and stearic acid. The use of stearic acid alone do not reduce tack. The amount of stearic acid is also important. As an example, ratio of 200 grams stearic acid to 2,000 gram of S-EB-S (a ratio of 0.1) will result in spotted tack reduction on the surface of the gel. A ratio of 250 to 2,000 will result in spotted crystallized stearic acid regions on the surface of the gel or spotted tack reduction. A ratio of 300 to 2,000 will result in complete tack reduction with large stearic acid crystallized regions on the surface of the gel. When microcrystalline waxes are incorporated together with stearic acid, the crystallization of stearic acid completely disappears from the surface of the gel. For example excellent result is achieved with 200 grams of stearic acid, 150 grams of microcrystalline wax and 2,000 grams of S-EB-S. The same excellent result is achieved when S-EB-S is adjusted to 3,000 grams, 4,000 grams, etc. The same result is achieved with (I) copolymers as well as in combination with polymers (II) such as SEPS, S-EB-EP-S, (S-EB-EP)$_n$, (SEB)$_n$, (SEP)$_n$ polymers. Moreover, when about 50 grams of tetrakis[methylene 3,-(3'5'-di-tertbutyl-4'-hydroxyphenyl) propionate] methane is use (per about 50 lbs of gel) as a tack reducing blooming agent, tack is completely removed from the surface of the gel after two to three weeks of blooming.

The fluffy crystal gels can also contain useful amounts of conventionally employed additives such as stabilizers, antioxidants, antiblocking agents, colorants, fragrances, flame retardants, flavors, other polymers in minor amounts and the like to an extend not affecting or substantially decreasing the desired properties. Additives in varying amounts useful in the gels of the present invention include: tetrakis[methylene 3,-(3'5'-di-tertbutyl-4"-hydroxyphenyl) propionate] methane, octadecyl 3-(3",5"-di-tert-butyl-4"-hydroxyphenyl) propionate, distearyl-pentaerythritol-diproprionate, thiodiethylene bis-(3,5-ter-butyl-4-hydroxy) hydrocinnamate, (1,3,5-trimethyl-2,4,6-tris[3,5-di-tert-butyl-4-hydroxybenzyl] benzene), 4,4"-methylenebis(2,6-di-tert-butylphenol), steraric acid, oleic acid, stearamide, behenamide, oleamide, erucamide, N,N"-ethylenebisstearamide, N,N"-ethylenebisoleamide, sterryl erucamide, erucyl erucamide, oleyl palmitamide, stearyl stearamide, erucyl stearamide, calcium sterate, other metal sterates, waxes (e.g., polyethylene, polypropylene, microcrystalline, carnauba, paraffin, montan, candelilla, beeswax, ozokerite, ceresine, and the like), teflon (TFE, PTFE, PEA, FEP, etc), polysiloxane, etc. The fluffy crystal gel can also contain metallic pigments (aluminum and brass flakes), TiO2, mica, fluorescent dyes and pigments, phosphorescent pigments, aluminatrihydrate, antimony oxide, iron oxides (Fe$_3$O$_4$, -Fe$_2$O$_3$, etc.), iron cobalt oxides, chromium dioxide, iron, barium ferrite, strontium ferrite and other maGnetic particle materials, molybdenum, silicones, silicone fluids, lake pigments, aluminates, ceramic pigments, ironblues, ultramarines, phthalocynines, azo pigments, carbon blacks, silicon dioxide, silica, clay, feldspar, glass microspheres, barium ferrite, wollastonite and the like. The

report of the committee ⬤ Gnetic Materials, Publication NMAB ⬤ National Academy Press (1985) is incorporated herein by reference.

The fluffy gels can be made into composites. The gels can be casted unto, pressured molded, injection molded and various methods of forming with or interlocking with various substrates, such as open cell materials, metals, ceramics, glasses, and plastics, elastomers, fluropolymers, expanded fluropolymers, Teflon (TFE, PTFE, PEA, FEP, etc), expanded Teflon, spongy expanded nylon, etc.; the molten crystal gel is deformed as it is being cooled. Useful open-cell plastics include: polyamides, polyimides, polyesters, polyisocyanurates, polyisocyanates, polyurethanes, poly(vinyl alcohol), etc. Suitable open-celled Plastic (sponges) are described in "Expanded Plastics and Related Products", Chemical Technology Review No. 221, Noyes Data Corp., 1983, and " Applied Polymer Science", Organic Coatings and Plastic Chemistry, 1975. These publications are incorporated herein by reference.

Not only are the $(G_n M_m)$ useful for insulating the body and selectively prevent generation of body moisture, sandwiches of fluffy gel-material, fluffy gel-material-fluffy gel or material-fluffy gel-material are useful as shock absorbers, acoustical isolators, vibration dampers, vibration isolators, and wrappers. For example the vibration isolators can be use under research microscopes, office equipment, tables, and the like to remove background vibrations. The tear resistance nature of the instant fluffy crystal gels are superior in performance to fluffy amorphous gels which are much less resistance to crack propagation caused by long term continue dynamic loadings.

The fluffy gel articles can be formed by blending, injection molding, extruding, spinning, casting, dipping and other conventional methods. For example, Shapes having various cross-section can be extruded. The fluffy crystal gels can also be formed directly into articles or remelted in any suitable hot melt applicator and extruded into shaped articles and films or spun into threads, strips, bands, yarns, or other shapes.

The fluffy gels are excellent for cast, injection, or spinning molding and the molded products have high tear resistance characteristics which cannot be anticipated form the properties of the raw components. Other conventional methods of forming the composition can be utilized.

It is found that orientation substantially affects the properties of the fluffy gels as well as non-fluffy gels made from the (I) copolymers of the invention. A non-fluffy gel is a gel which is void of the microsphere particulate dispersion of the fluffy gels. In other words a plain optically clear gel. The effect of orientation is noted as follows: when a optically clear gel is extruded by conventional means, such as under high pressure or experience extreme high tension and extension while being rapidly cooled, the gel may become tough in the radial direction and very weak in the transverse direction. This may be because in rapid extension and cooling of the melt or molten gel, the styrene domains forms clyinderically along the transverse axis in the solid state and is very weak under tension. It may be possible to cure this weakness by annealing the extruded gel at or near the polystyrene melting point. On the other hand, When an optically clear gel is extruded by a rotating cone or plate elastic energy method of extrusion, the extruded gel can also become highly oriented, but in the radial direction which results in a very strong gel when extended in the transverse direction as well as a tough gel in the radial direction. Consequently, oriented fluffy gels can be very weak or strong depending of the methods selected for making articles from such fluffy gels.

Not only do the fluffy gels have all the desirable combination of physical and mechanical

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properties substantially ███ lar to high viscosity amorphous S-█ ███ gels such as high elongation at break of at least 1,600%, ultimate tensile strength of about 8×10^5 dyne/cm^2 and higher, low elongation set at break of substantially not greater than about 2%, substantially about 100% snap back when extended to 1,200% elongation, and a gel rigidity of substantially from about 2 gram to about 3,000 gram Bloom and higher, the fluffy gels of the present invention exhibit improved tear resistance and resistance to fatigue not obtainable from amorphous S-EB-S or S-EP-S gels at corresponding gel rigidities.

The fluffy gels of the present invention exhibit one or more of the following properties. These are: (1) tensile strength of about from less than about 8×10^5 dyne/cm^2 to about 10^7 dyne/cm^2 and greater; (2) elongation of less than about 200% to about 3,000% and higher; (3) elasticity modules of less than about 10^4 dyne/cm^2 to about 10^6 dyne/cm^2 and greater; (4) shear modules of less than about 10^4 dyne/cm^2 to about 10^6 dyne/cm^2 and greater as measured with a 1, 2, and 3 kilogram load at 23°C; (5) gel rigidity of about less than about 2 gram Bloom to about 3,000 gram Bloom and higher as measured by the gram weight required to depress a gel a distance of 4 mm with a piston having a cross-sectional area of 1 square cm at 23°C; (6) tear propagation resistance from less than about 1.5 kg/cm to about 5.6 kg/cm or higher (the tear resistance of fluffy crystal gels being advantageously greater than that of fluffy amorphous gels); (7) resistance of the fluffy crystal gels to fatigue being advantageously greater than the fatigue resistance of fluffy amorphous gels at corresponding gel rigidities; (8) and substantially 100% snap back recovery when extended at a crosshead separation speed of 25 cm/minute to 200% at 23°C. Properties (1), (2), (3), and (6) above are measured at a crosshead separation speed of 25 cm/minute at 23°C.

The molded fluffy crystal (-E- midblock segment) gel articles have additional important advantages in that the end-use performance properties are advantageously greater than amorphous -EB- and -EP- midblock segment block copolymer gels in that they are more resistant to cracking, tearing, crazing or rupture in flexural, tension, compression, or other deforming conditions of use. Like amorphous gels, the molded articles made from the instant composition possess the intrinsic properties of elastic memory enabling the articles to recover and retain its original molded shape after many extreme deformation cycles.

Not only is the fluffy gels of the invention advantageous for use in making toys, the novel fluffy crystal gels because of their improved properties find other piratical uses. Because of their improved tear resistance and improved resistance to fatigue, the fluffy crystal gels of the present invention achieve greater performance than amorphous gels in low frequency vibration applications, such as viscoelastic layers in constrained-layer damping of mechanical structures and goods, as viscoelastic layers used in laminates for isolation of acoustical and mechanical noise, as anti-vibration elastic support for transporting shock sensitive loads, as vibration isolators for an optical table, as viscoelastic layers used in wrappings, enclosures and linings to control sound, as compositions for use in shock and dielectric encapsulation of optical, electrical, and electronic components.

Because of their improved tear resistance and improved resistance to fatigue, the fluffy crystal gels are more useful as molded shape articles for use in medical and sport health care, such use include therapeutic hand exercising grips, dental floss, crutch cushions, cervical pillows, bed wedge pillows, leg rest, neck cushion, mattress, bed pads, elbow padding, dermal pads, wheelchair

cushions, helmet liner, ● and hot packs, exercise weight belt ● raction pads and belts, cushions for splints, slings, and braces (for the hand, wrist, finger, forearm, knee, leg, clavicle, shoulder, foot, ankle, neck, back, rib, etc.), and also soles for orthopedic shoes. Other uses include various shaped articles as toys, as tips for swabs, as fishing bate, as a high vacuum seal (against atmosphere pressure) which contains a useful amount of a mineral oil-based maGnetic fluid particles, etc. Moreover, the casted, extruded, or spun threads, strips, yarns, tapes can be weaved into cloths, fine or coarse fabrics.

The fluffy gels can be formed in any shape; the original shape can be deformed into another shape (to contact a regular or irregular surface) by pressure and upon removal of the applied pressure, the composition in the deformed shape will recover back to its original shape.

As an example of the versatility of use of the instant fluffy crystal gels, a hand exerciser can be made in any shape so long as it is suitable for use as a hand exerciser: a sphere shape, a cube shape, a rectangular shape, etc. Likewise, a wheelchair cushion can be made from the composition in any shape, so long as it meets the needs of the user of the cushion. For example, a cushion can be made by forming the composition into a selected shape matching the contours of the specific body part or body region. The composition can be formed into any desired shaped, size and thickness suitable as a cushion; the shaped composition can be additionally surrounded with film, fabric, other foams, or any other desired material or combinations thereof. Moreover, the composition can be casted onto such materials, provided such materials substantially maintain their integrity (shape, appearance, texture, etc.) during the casting process. The same applies for brace cushions, liners, linings and protective coverings for the hand, wrist, finger, forearm, knee, leg, and the like having highly reduce weight. The fluffy gels are advantageously useful as cushions, liners, and coverings which interfaces the body or parts of the body with artificial devices.

Because of their improved tear resistance and resistance to fatigue, the fluffy crystal gels exhibit versatility as materials formed into hollowed thick wall body shapes for use in deep sea ice water diving or insulating the body from extreme cold. Since the fluffy crystal gels are more tear resistant, they are especially useful for making toys and balloons, and insulating gloves. As toy balloons, the fluffy crystal gels are safer because it will not rupture or explode when punctured as would latex balloons which often times cause injures or death to children by choking from pieces of latex rubber. The fluffy crystal gels are advantageously useful for making one layer gloves for vibration damping which prevents damage to blood capillaries in the fingers and hand caused by handling strong shock and vibrating equipment.

Other uses include self sealing enclosures for splicing electrical and telephone cables and wires. For example, the fluffy crystal gels can be pre-formed into a small diameter tubing within an outer elastic tubing, both the internal fluffy crystal gel tubing and external elastic tubing can be axially expanded and fixed in place by a removable continuous retainer. Upon insertion of a spliced pair or bundle of cables or wires, the retainer can be removed, as the retainer is removed, the fluffy crystal gel and elastic tubing impinges onto the inserted cables or wires splices, thereby sealing the electrical splices against weather, water, dirt, corrosives and shielding the splice from external abuse. The enclosure is completed without the use of heat or flame as is conventionally performed.

In all cases, the tear strength of fluffy crystal gels are higher than that of amorphous

gels. For example, the f⬤y crystal gels made from high visco⬤S-E-EB-S and S-E-EP-S copolymers are resistant to tearing when sheared than high viscosity amorphous S-EB-S and S-EP-S copolymer gels. This can be demonstrated by forming a very soft gel samples, for example 100 parts copolymer to 800 parts plasticizing oil. The soft gel is made in a 16 mm X 150 mm test tube, the gel cylinder is cut or notched at one point about its cross-section and gripped lengthwise tightly in the left hand about this cross-section point and a length of exposed gel is gripped lengthwise around the adjacent cross-section point tightly by the right hand as close to the left hand as possible without stretching. With the two hands gripping the gel sample's cross-section about the notched point, the hands are moved in opposite directions to tear apart the gel sample at the cross-section point. The shearing action by the gripping hands is done at the fastest speed possible as can be performed by human hands. Using this demonstration, the fluffy crystal gels will not easily break or tear completely apart, whereas, amorphous S-EB-S and S-EP-S gels break or tears apart easily. Likewise the various fluffy crystal gels of the invention described herein are tested and found to be more tear resistant than fluffy amorphous gels. For toys such as airfoils, the improved lower density and resistance to tearing are essential for acceptable performance during play.

The invention is further illustrated by means of the following illustrative embodiments, which are given for purpose of illustration only and are not meant to limit the invention to the particular components and amounts disclosed.

EXAMPLE I

Unexpanded methacrylonitrile microspheres #051, #053, #091, #091-80, and #092-120 as obtained from Expandcel, In., are dispersed in Duraprime 70 white oil in varying amounts to yield oil/microsphere mixtures having the following approximate viscosities (poise): 0.5, .8, 1.5, 18, 34, 100, 150, 250, 400, 460, 480, 560, 720, 1000, and 2000.

EXAMPLE II

Gels of 100 parts of high viscosity linear amorphous S-EB-S (Kraton G1651) block copolymer and 1,600, 1,200, 1,000, 800, 600, 500, 450, 300, 250 parts by weight of Duraprime 70 white oil (plasticizer) are melt blended in an anchor mixer to obtain clear molten gels at selected temperatures and viscosities which are dependent on the parts by weight of oil and resultant molten viscosity (as denoted by: parts oil/temperature °F/-poise) as follows: 1,600 @275°F/-15-30 poise, 1,200 @280°F/-18-25 poise, 1,000 @300°F/-20-35 poise, 800 @310°F/-30-60 poise, 600 @325°F/-50-120 poise, 500 @350°F/-100-300 poise, 450 @375°F/-150-400 poise, 300 @400°F/-200-400 poise, and 250 @425°F/-300-500 poise.

EXAMPLE III

Gels of 100 parts of high viscosity linear Kuraray SEPTON 2006 (amorphous S-EP-S) block copolymer and 1,600, 1,200, 1,000, 800, 600, 500, 450, 300, 250 parts by weight of Duraprime 70 white oil (plasticizer) are melt blended in an anchor mixer to obtain clear molten gels at selected temperatures and viscosities which are dependent on the parts by weight of oil and resultant molten viscosity (as denoted by: parts oil/temperature °F/-poise) as follows: 1,600 @275°F/-15-30 poise,

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1,200 @280°F/-18-25 pois⬤000 @300°F/-20-35 poise, 800 @310°⬤60 poise, 600 @325°F/-50-120 poise, 500 @350°F/-100-300 poise, 450 @375°F/-150-400 poise, 300 @400°F/-200-400 poise, and 250 @425°F/-300-500 poise.

Note: As the viscosity of the oil used is increase (from Duraprime 70 to 200, 300, 350, 400, etc.) so will the resultant viscosities of the oil/unexpanded thermoplastic particular mixtures and the molten gel viscosities change. As the oil viscosity is increased, the tack of the fluffy gels will increase substantially. The quantity and viscosity of the particulate mixtures of Examples I selected for dispersion in the molten gels of Examples II and III depends on the final fluffy gel density desired and the molten gel viscosity and temperature as well as the approximate amount of time necessary for adequate dispersion of the particulate mixture in the molten gel.

EXAMPLE IV

Step 1: Determine the amounts of unexpanded particulate/oil mixture needed to yield the desired fluffy gel densities and match the viscosity of the mixtures of Examples I with the viscosities of the molten gels of Examples II and III. Step 2: add additional amounts of component II as necessary to the matched Example I mixture selected to obtain the particulate dispersion time (mixing time) required based on the temperatures and viscosities of the molten gels of Examples II and III {i.e., $1/10(t_u)$, $1/5(t_u)$, $1/3(t_u)$, $1/4(t_u)$, $1/2(t_u)$, and (t_u), etc.,}. Step 3: while continuing heating and mixing the molten gels of Examples II and III, add the selected amounts of unexpanded particulate/oil mixtures. Step 4: pressed, molded and extruded into various forms and shapes the resulting fluffy gels at mixing temperatures above 250°F. Step 5: allow part of the fluffy gels to cool to room temperature and then formed it into articles by reheating the fluffy gels above 300°F under pressure. The fluffy gels and articles made by this procedure are found to exhibit adequate uniform dispersion of the expanded microspheres for densities of about 0.7 g/cm^3, 0.65 g/cm^3, 0.60 g/cm^3, 0.55 g/cm^3, 0.50 g/cm^3, 0.45 g/cm^3, 0.40 g/cm^3, 0.35 g/cm^3, 0.30 g/cm^3, and 0.28 g/cm^3. The fluffy gels are found to exhibit gel rigidities of from about 20 to about 3,000 gram Bloom, and elongations of at least 200%.

EXAMPLE V

Procedures of Example IV is repeated using high viscosity crystalline midblock segment linear S-E-EB-S and (S-E-EB)$_n$ multi-arm block copolymers (n = 2, 3, 4, and 5) with ethylene to ethylene/butylene midblock ratios (E:EB) of 89:11, 88:12, 87:13, 86:14, 85:15, 84:16, 83:17, 82:18, 81:19, 80:20, 79:21, 78:22, 77:23, 76:24, 75:25, 74:26, 73:27, 72:28, 71:29, and 70:30. It is found the procedure of the Example is capable of producing fluffy gels of about 0.6 g/cm^3 to about 0.30 g/cm^3, gel rigidities of from about 20 to about 3,000 gram Bloom, elongations of at least 200%, and the tensile strength, notched tear strength, and resistance to fatigue are found to be greater than that of fluffy amorphous gels of Examples IV.

EXAMPLE VI

Procedures of Example IV is repeated using high viscosity crystalline midblock segment linear S-E-EP-S and radial (S-E-EP)$_n$ multi-arm block copolymers. It is found the procedure of the Example is

capable of producing flu██ gels of about 0.6 g/cm^3 to about 0.██ cm^3, gel rigidities of from about 20 to about 3,000 gram Bloom, elongations of at least 200%, and the tensile strength, notched tear strength, and resistance to fatigue are found to be greater than that of fluffy amorphous gels of Examples IV.

EXAMPLE VII

Procedures of Example IV is repeated using high viscosity crystalline midblock segment linear (S-B-S), (S-B-EP-S), (S-B-EB-S), (S-B-EP-B-S), (S-B-EB-B-S), (S-B-EB-EP-S), (S-B-EP-EB-S), (S-EB-EP-S), (S-EP-B-EP-S), (S-B-EB-B-EB-S), (S-B-EB-B-EP-S) and (S-B-EP-B-EP-B-S) block copolymers. It is found the procedure of the Example is capable of producing fluffy gels of about 0.6 g/cm^3 to about 0.30 g/cm^3, gel rigidities of from about 20 to about 3,000 gram Bloom, elongations of at least 200%, and the tensile strength, notched tear strength, and resistance to fatigue are found to be lower than that of fluffy crystal gels of Examples V and VI.

EXAMPLE VIII

Example IV is repeated using high viscosity crystalline midblock segment linear (S-E-EB$_{25}$-S), (S-EP-E-EP-S), (S-E-EB-S), (S-E-EP-S), (S-E-EP-E-S), (S-E-EB-B-S), (S-E-B-EB-S), (S-E-B-EP-S), (S-E-EB-EP-S), (S-E-EP-EB-S), (S-E-EP-E-EP-S), (S-E-EP-E-EB-S), (S-E-EB-B-EP-S), (S-E-EP-B-EB-S), (S-E-EP-E-EP-E-S), (S-E-EP-E-EB-S), (S-E-EP-E-EP-EB-S), (S-E-EP-E-EP-E-S), and (S-E-EP-EB-EP-EB-B-S) block copolymers. It is found the procedure of the Example is capable of producing fluffy gels of about 0.6 g/cm^3 to about 0.30 g/cm^3, gel rigidities of from about 20 to about 3,000 gram Bloom, elongations of at least 200%, and the tensile strength, notched tear strength, and resistance to fatigue are found to be greater than that of amorphous gels of Example IV.

EXAMPLE IX

Example IV is repeated using high viscosity polyurethane elastomers formed from a hydroxyl terminated poly(ethylene-butylene) oligomer having TMP/diisocyanate and BEPD/diisocyanate copolymer crystalline groups. The fluffy polyurethane elastomer gels are formed at between about 375°C to about 450°C. It is found the procedure of the Example is capable of producing fluffy gels of about 0.6 g/cm^3 to about 0.30 g/cm^3, gel rigidities of from about 20 to about 3,000 gram Bloom, elongations of at least 200%, and the tensile strength, notched tear strength, and resistance to fatigue are found to be greater than that of amorphous gels of Example IV.

EXAMPLE X

Example IV is repeated using high viscosity crystalline midblock segment multiarm (S-E-EB)$_n$, (S-E-EP)$_n$, (S-E-EP-E)$_n$, (S-E-EB-B)$_n$, S-E-B-EB)$_n$, (S-E-B-EP)$_n$, (S-E-EB-EP)$_n$, (S-E-EP-EB)$_n$, (S-E-EP-E-EP)$_n$, (S-E-EP-E-EB)$_n$, (S-E-EB-B-EP)$_n$, (S-E-EP-B-EB)n, (S-E-EP-E-EP-E)n, (S-E-EP-E-EB)n, (S-E-EP-E-EP-EB)n, (S-E-EP-E-EP-E)n, and (S-E-EP-EB-EP-EB-B)n, with n = 2, 3, 4, and 5 block copolymers. It is found the procedure of the Example is capable of producing fluffy gels of about 0.6 g/cm^3 to about 0.30 g/cm^3, gel rigidities of from about 20 to about 3,000 gram Bloom, elongations of at least 200%, and the tensile strength, notched tear strength, and resistance to fatigue are found to be greater than that of amorphous gels of Example IV.

ethylene-styrene), poly(■■■ne-butylene-styrene), poly(styrene-■■■lene-ethylene/butylene-styrene),
poly(styrene-ethylene-ethylene/propylene-styrene), poly(styrene-butylene-ethylene/propylene-
styrene), poly(styrene-butylene-ethylene/butylene-styrene), poly(styrene-ethylene-
ethylene/propylene-ethylene-styrene), poly(styrene-ethylene-ethylene/butylene-butylene-styrene),
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ethylene-ethylene/butylene)$_n$, poly(styrene-ethylene/propylene-butylene-ethylene/propylene)$_n$,
poly(styrene-butylene-ethylene/butylene-butylene-ethylene/butylene)$_n$, poly(styrene-butylene-
ethylene/butylene-butylene-ethylene/propylene)$_n$, poly(styrene-ethylene-ethylene/butylene-butylene-
ethylene/propylene)$_n$, poly(styrene-ethylene-ethylene/propylene-butylene-ethylene/butylene)$_n$,
poly(styrene-ethylene-ethylene/propylene-ethylene-ethylene/propylene-ethylene)$_n$, poly(styrene-
butylene-ethylene/propylene-butylene-ethylene/propylene-butylene)$_n$, poly(styrene-ethylene-

ethylene/propylene-ethyl⬤ethylene/butylene)$_n$, poly(styrene-et⬤ne-ethylene/propylene-ethylene-ethylene/propylene-ethylene/butylene)$_n$, poly(styrene-ethylene-ethylene/propylene-ethylene-ethylene/propylene-ethylene)$_n$, poly(styrene-ethylene-ethylene/propylene-ethylene/butylene-ethylene/propylene-ethylene/butylene-butylene)$_n$ or a mixture thereof.

3.   A gel according to claim 1, wherein said (IV) polar polymer is ethylene-butyl acrylate, ethylene-ethyl acrylate, ethylene-methyl acrylate, ethylene-vinyl acetate, ethylene-vinyl acrylate, ethylene-vinyl alcohol, acrylonitrile-styrene-acrylate, styrene-acrylonitrile, styrene-maleic anhydride, meleated poly(styrene-ethylene-propylene-styrene), meleated poly(styrene-ethylene-butylene-styrene) or a mixture thereof.

4.   A gel according to claim 1, wherein said selected (V) crystalline or non-crystalline polymer or copolymer is poly(styrene-butadiene-styrene), poly(styrene-butadiene), poly(styrene-isoprene-styrene), poly(styrene-isoprene), poly(styrene-ethylene- propylene), low viscosity poly(styrene-ethylene- propylene-styrene), low viscosity poly(styrene-ethylene-butylene- styrene), poly(styrene- ethylene-butylene), meleated poly(styrene-ethylene-butylene-styrene), high vinyl content poly(styrene-ethylene- butylene-styrene), poly(styrene-ethylene-propylene-styrene-ethylene-propylene), poly(ethylene-propylene), poly(styrene-butadiene)$_n$, poly(styrene-butadiene)n, poly(styrene-isoprene)$_n$, poly(styrene-isoprene)$_n$, poly(styrene-ethylene-propylene)$_n$, low viscosity poly(styrene-ethylene-propylene)$_n$, low viscosity poly(styrene-ethylene-butylene)$_n$, poly(styrene-ethylene-butylene)$_n$, meleated poly(styrene-ethylene-butylene)$_n$, high vinyl content poly(styrene-ethylene-butylene)$_n$, poly(styrene-ethylene-propylene-styrene-ethylene-propylene)$_n$, poly(ethylene-propylene)$_n$, polystyrene, polybutylene, poly(ethylene-propylene), poly(ethylene-butylene), polypropylene, polyethylene, polypthalamide or polyurethane elastomer formed from one or more saturated hydrocarbon diols, wherein said selected block copolymer is a linear, branched, multiarm, or star shaped copolymer.

5.   A gel according to claim 1, wherein said (I) copolymer of said gel is a thermoplastic polyurethane elastomer made with diisocyanates and chain extenders 2,2,4-trimethyl-1,3-pentancdiol or 2-Butyl-2-ethyl-1,3-pentanediol and a saturated hydrocarbon diol, said polyurethane having one or more crystalline groups of about 22% to about 45% wy weight of said elastomer and capable of exhibiting a glass transition of at least about -40°C.

6.   A gel according to claim 10, wherein said hydrocarbon diols is a hydroxyl terminated oligomer of poly(ethylene-butylene) or poly(ethylene-propylene).

7.   A cold weather sock for footwear formed of a gel composite of claim 1, for direct contact with the foot and capable of substantially preventing the generation moisture from said foot.

8.   A cold wea⬤ footwear having an outer boot, a p⬤med sock disposed in said boot and formed of a gel composite according to claim 1 for direct contact with the foot and capable of substantially preventing the generation moisture from said foot.

9.   A cold weather face mask for protection of the head, face, and neck areas against low temperatures and high wind velocities made from the gel composite of claim 1 for direct contact with the head, face, and neck and capable of substantially preventing the generation moisture from said head, face, and neck and having openings for insertion and removal of one or more hydrophilic patches in selected areas covered by said mask.

10.   A cold weather body suit for protection of the body areas against low temperatures and high wind velocities made from the gel composite of claim 1 for direct contact with the body and capable of substantially preventing the generation moisture from said body and having openings for insertion and removal of one or more hydrophilic patches in selected areas of the body covered by said suit.